



CAS-ISSP The Second RCM of the CRP on Irradiated W



Retention and diffusion of hydrogen in tungsten: effects of temperature, alloying elements and vacancy clusters

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1. Background and research plan

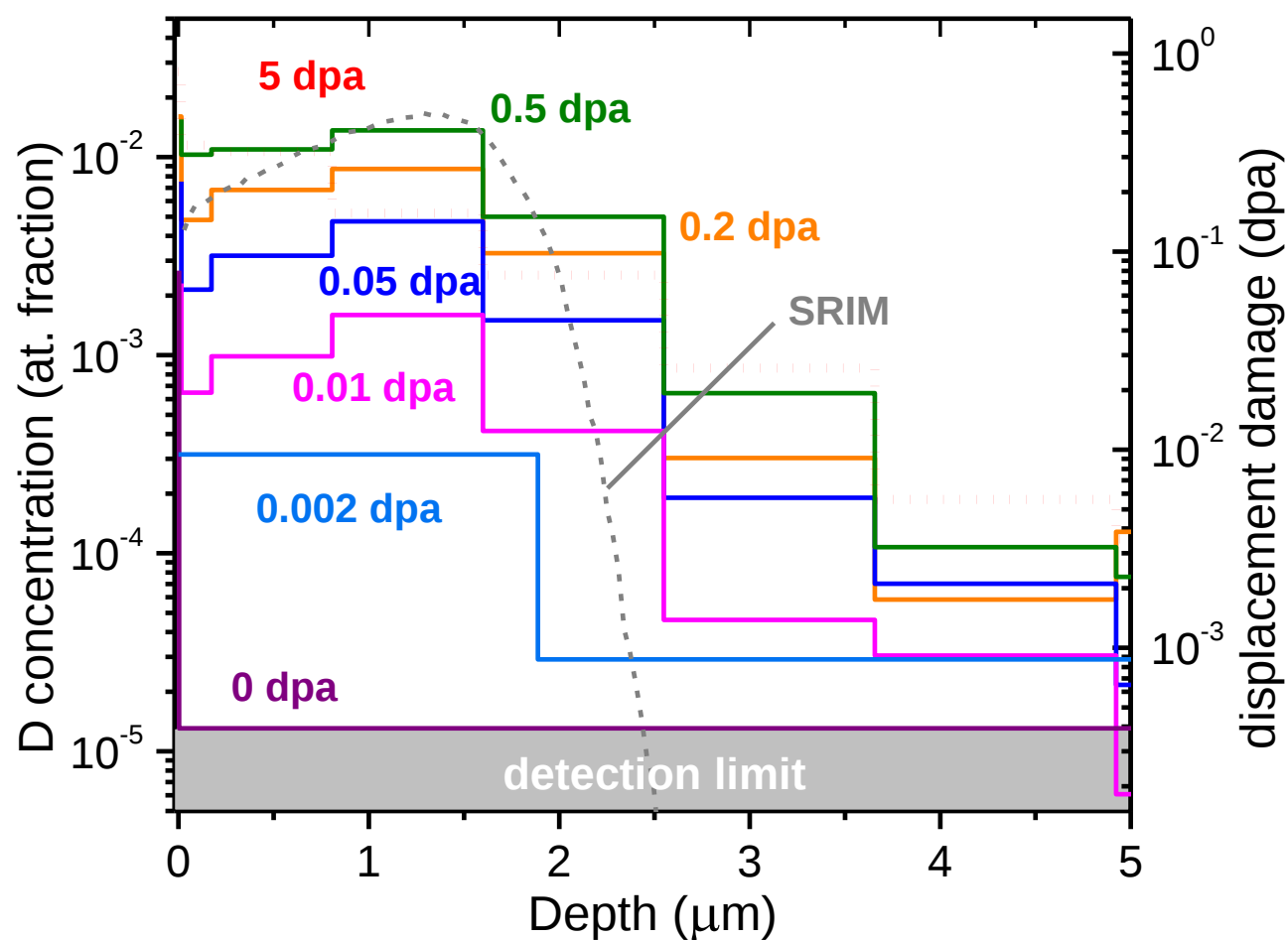
2. Research results

- First-principles calculations of hydrogen solution and diffusion in tungsten: Temperature and defect-trapping effects.
- First-principles calculations of transition-metal solute interactions with point defect and hydrogen in tungsten.

3. Ongoing work

- OKMC modelling on the hydrogen retention and desorption in tungsten

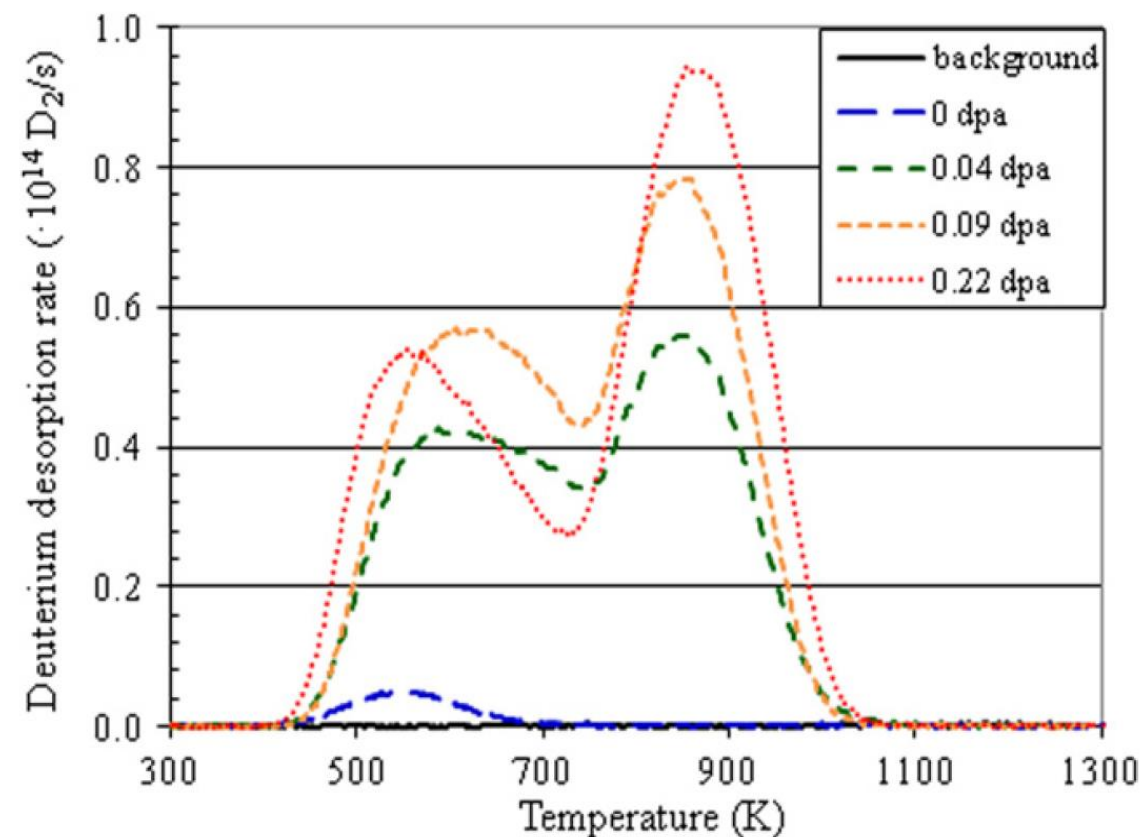
1. Backgrounds: Deuterium retention



- Hydrogen retention in natural W:
0.001 – 0.01% at ≤ 450 K
- Displacement damage increases
hydrogen retention to 1.5% at 450 K
 $\Rightarrow$ In the presence of neutrons
retention is dominated by damage

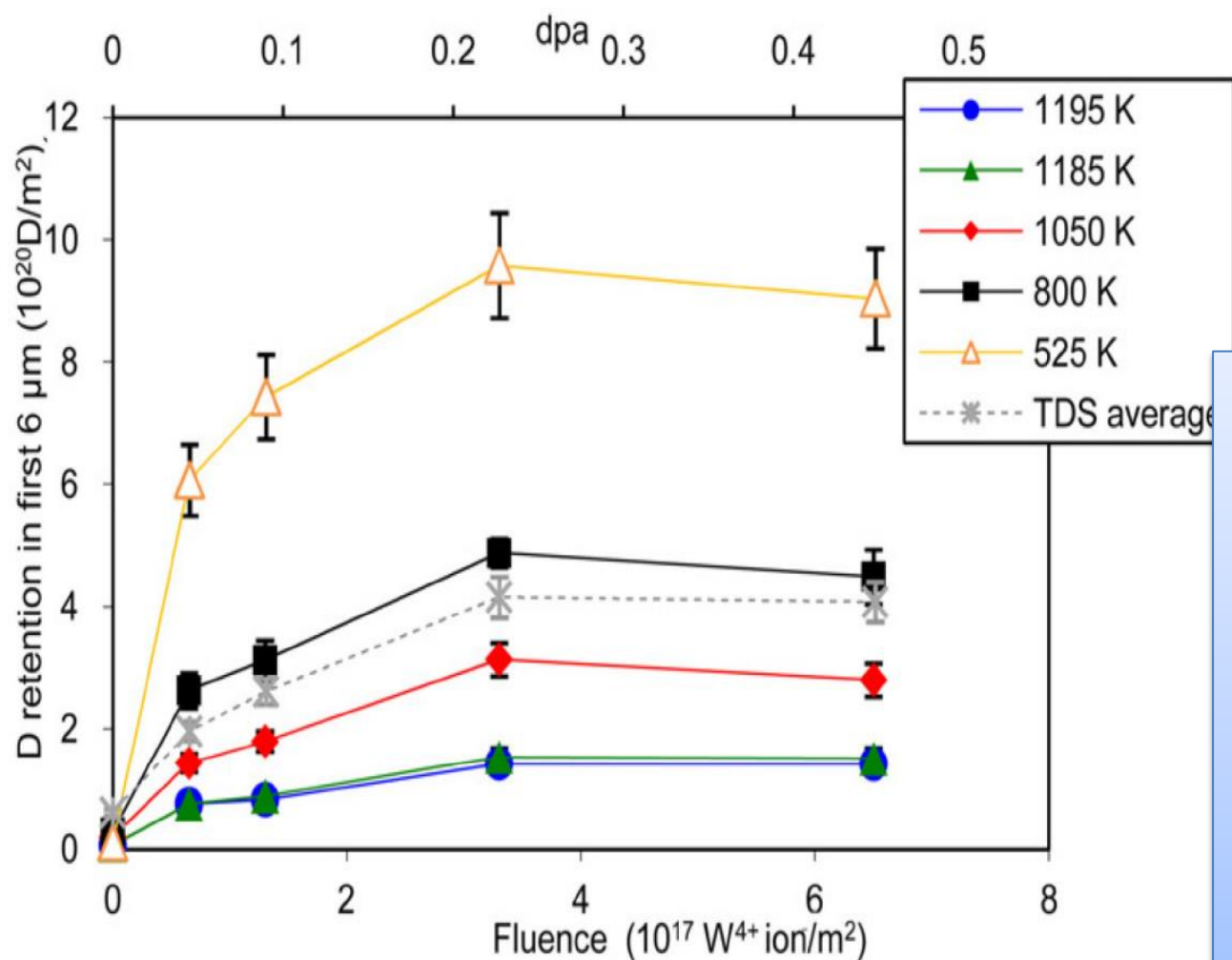
1. Backgrounds: deuterium retained in damaged W

Thermal desorption spectra



- Pre-irradiation enhances the intensity of the low temperature peak and introduces a high temperature peak at about 850 K.
- The low temperature peak, caused by deuterium trapped in intrinsic defects, is usually associated with dislocations, grain boundaries, and single vacancies.
- The high temperature peak is usually associated with deuterium trapped in vacancy clusters.

1. Backgrounds: deuterium retained in damaged W

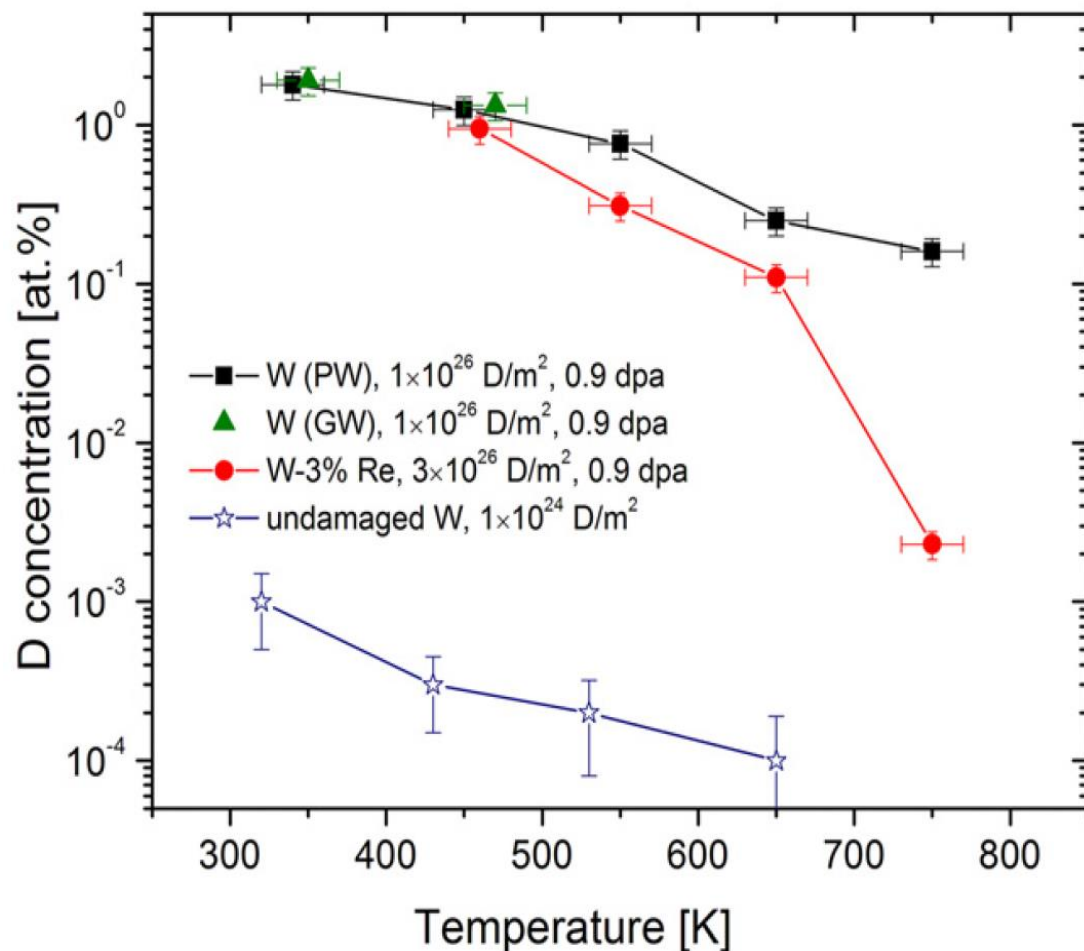


- The D retention shows saturation at the damage level of about 0.25 dpa.
- The D retention is strongly reduced at high temperatures of 800-1200 K compared with that at 525K.

The integrated amount of retained deuterium as a function of pre-irradiation fluence. Targets were exposed at different temperatures

1. Backgrounds: deuterium retained in damaged W-Re

B. Tyburska-Püuschel et al. Nucl. Fusion 53 (2013) 123021

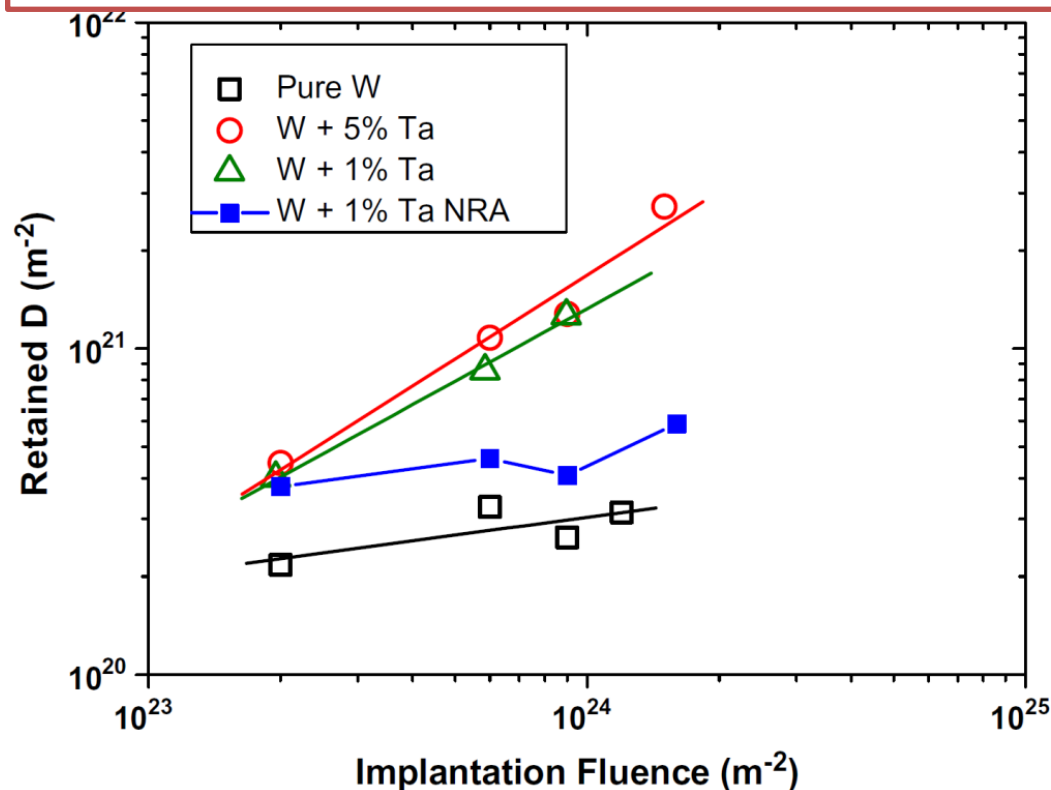


- The concentration of deuterium retained in the tungsten-ion-induced damage zone decreases with increasing exposure temperature .
- Adding Re into W leads to a decrease of the D concentration at exposure temperatures above 450K.
- It drops significantly faster in W-Re than in pure W, given sufficiently high temperatures.

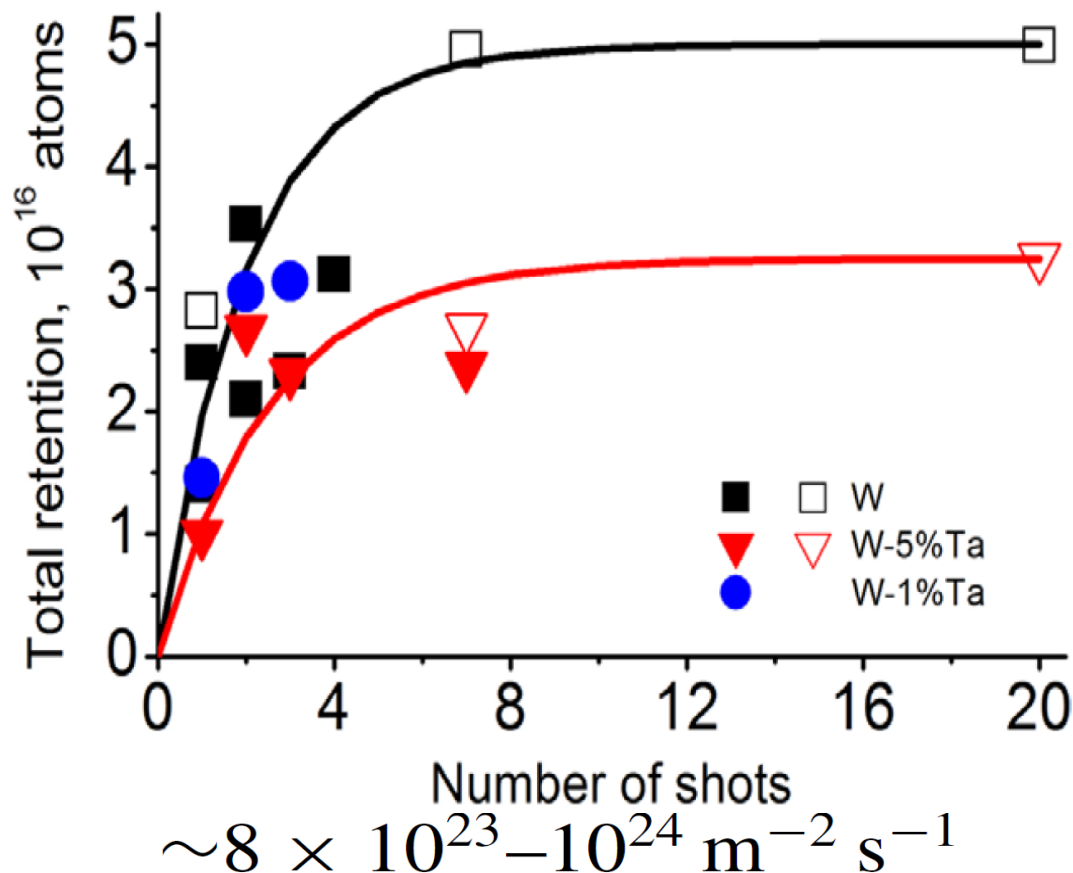
Note that:

Similar changes in retention behavior were not observed in undamaged samples.

K. Schmid et al. J. Nucl. Mater. 426(2012)247



Y. Zayachuk et al Nucl. Fusion 53 (2013)013013



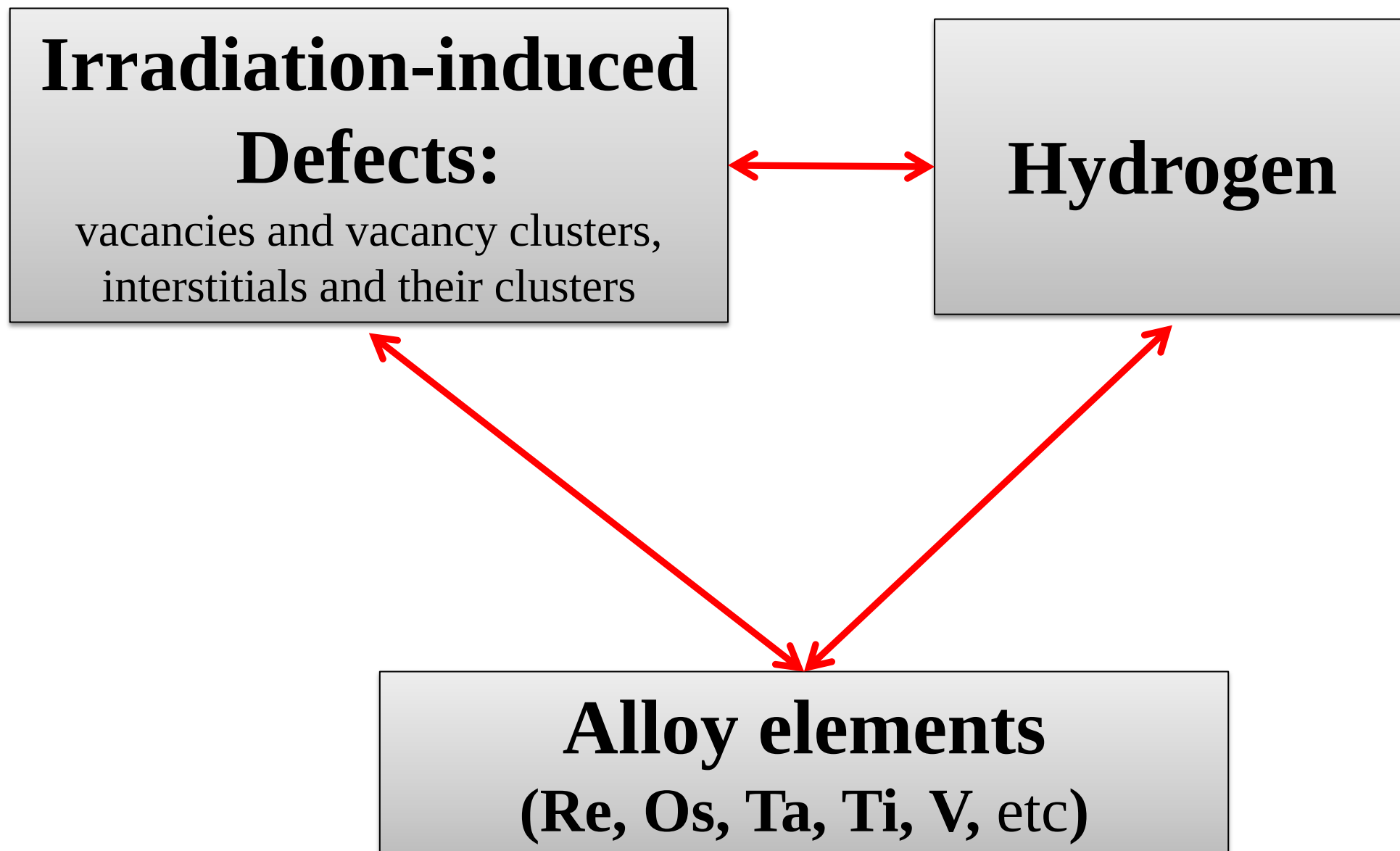
Ion fluxes $\sim 10^{19} \text{ m}^{-2} \text{ s}^{-1}$

$\sim 8 \times 10^{23} - 10^{24} \text{ m}^{-2} \text{ s}^{-1}$

In the **low fluxes** conditions, the deuterium retention in W-Ta was significantly **higher** than in W

In the **high fluxes** conditions, deuterium retention was systematically **lower** in W-Ta than in W..

1. Backgrounds: Hydrogen retention in damaged W and W-alloy



The energetic and dynamic behavior of defects



Statistical analysis of thermodynamics

The synergetic effects of the defect, hydrogen and alloy elements

The formation energy, migration barrier, jumping frequency of the defects, the interactions among hydrogen and alloy elements and defects: their binding energy and interaction radius, dissolution/detrapping energy.

The energetic and dynamic behavior of defects

Statistical analysis of thermodynamics

The synergistic effects of the defect, hydrogen and alloy elements



These energetic and dynamic parameters are used as input to the thermodynamic model to evaluate the influence of irradiation defects and alloying elements on the hydrogen diffusion and release.

The energetic and dynamic behavior of defects

Statistical analysis of thermodynamics

The synergetic effects of the defect, alloy elements and hydrogen



Based on the above results, we build the defects and their interaction model, and then investigate the long-term (in hour) synergistic effects of irradiation defects, alloying elements and hydrogen in large system (in micron) by object kinetic Monte Carlo.

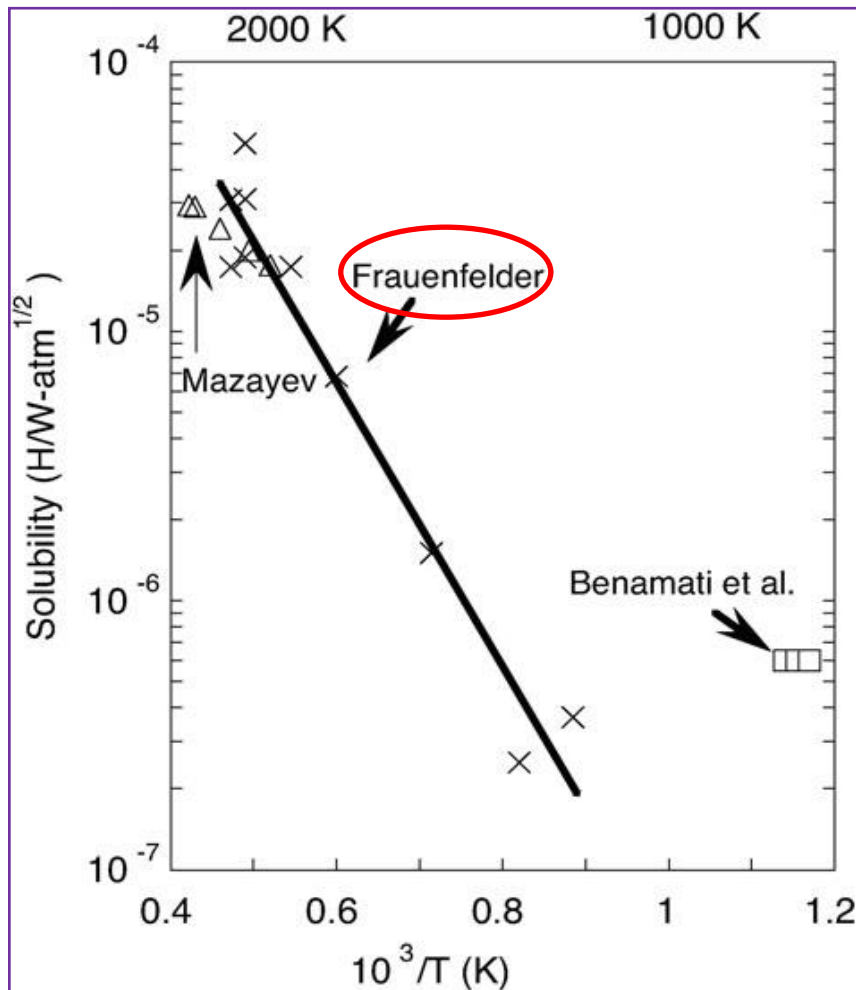
- **First-principles calculations of hydrogen solution and diffusion in tungsten: Temperature and defect-trapping effects. ([Acta Materialia 84 \(2015\) 426–435](#))**
- **First-principles calculations of transition-metal solute interactions with point defect and hydrogen in tungsten. ([Acta Materialia 66 \(2014\) 172–183](#), [Nuclear Fusion \(under review\)](#))**

Hydrogen solution and diffusion in tungsten: Temperature and defect-trapping effects.

In order to obtain the reliable solubility and diffusivity of hydrogen in tungsten.

Experimental data for hydrogen Solubility and diffusivity

Solubility and diffusivity of hydrogen in tungsten **are scarce and largely scattered**



- The absolute values of the solubility among these reported data are within the same order of magnitude.
- **But their pre-exponential factors and activation energies are completely different.** For example, the activation energies are 1.04, 0.03 and 0.19 eV.

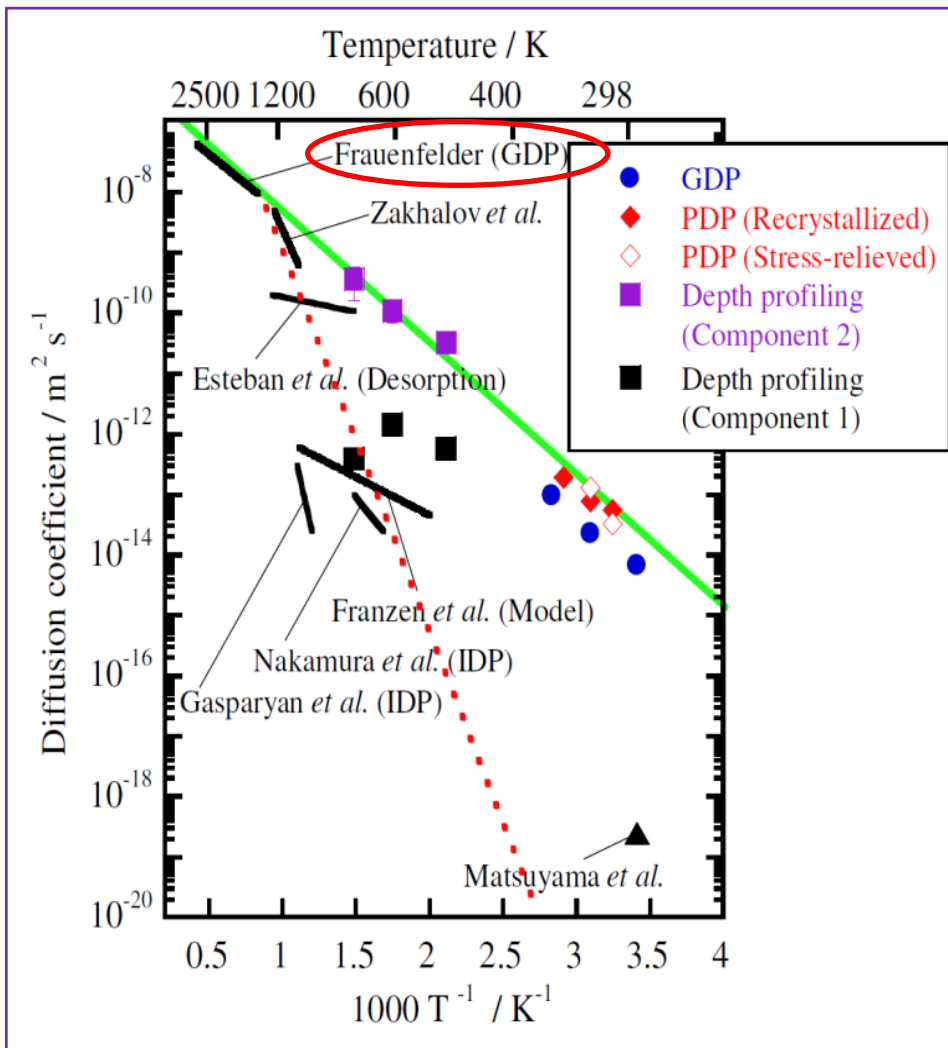
Frauenfelder (1100~2400 K)

$$S = 9.3 \times 10^{-3} \exp(-1.04 \text{ eV}/kT)$$

- Frauenfelder's data agrees well with Mazayev's measured data covering the temperature range 1900–2400 K.
- The extrapolation of Frauenfelder's data to lower temperatures is much lower than Benamati's data at 850 to 885 K.

Experimental data for hydrogen Solubility and diffusivity

Figure 4. Comparison of temperature dependence of H DCs in W determined by various authors; GDP and PDP (●, ◆, ◇) by Ikeda [55, 56], depth profiling 1 (■) and 2 (■) by Otsuka [56, 57] and Matsuyama [24], GDP by Frauenfelder [14], Zakharov [16] and Esteban [22], IDP by Gasparyan [23] and Nakamura [18], Model calculation by Franzen [20]. GDP, PDP and IDP stand for gas, plasma and ion driven permeation, respectively.



Among these experimental data, the data at high temperatures ($>1500\text{K}$), reported by Frauenfelder, has been usually believed to be the most reliable data, because it was obtained at elevated temperatures and is likely less influenced by both surface and trapping effects.

As an envelope of highest data so far reported, Ikeda and Otsuka proposed $D = 3.8 * 10^7 \exp(0.41 \text{ eV}/kT) \text{ m}^2/\text{s}$ (the green line in the figure) as the most reliable DC, which is valuable for a wide temperature range of 250–2500 K.

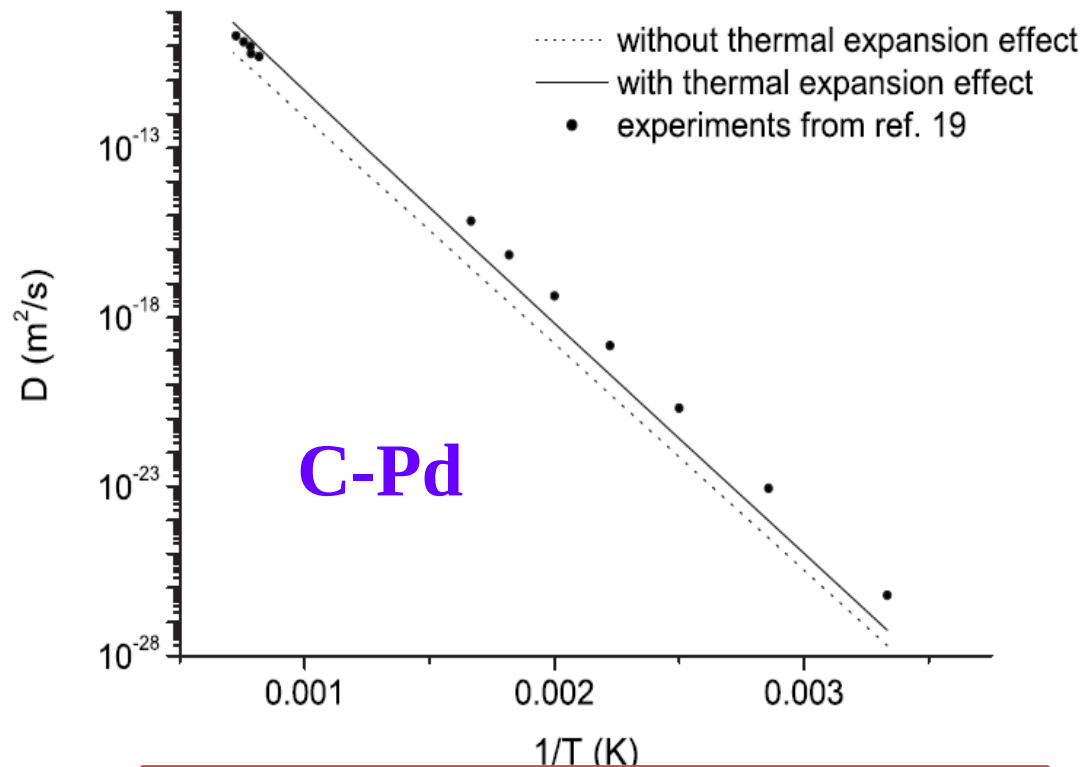
As summarized above, although various parameters for hydrogen solubility and diffusivity in tungsten have been recommended, some experimental values have been reported and moreover these parameters show large discrepancies. This is particularly true for the values of solution and activation energies.

These discrepancies may arise from the use of different techniques to obtain the data. In addition, the extremely low solubility of hydrogen in tungsten and the significant surface and trapping effects make the experimental measurements difficult and complex, particularly at low temperatures.

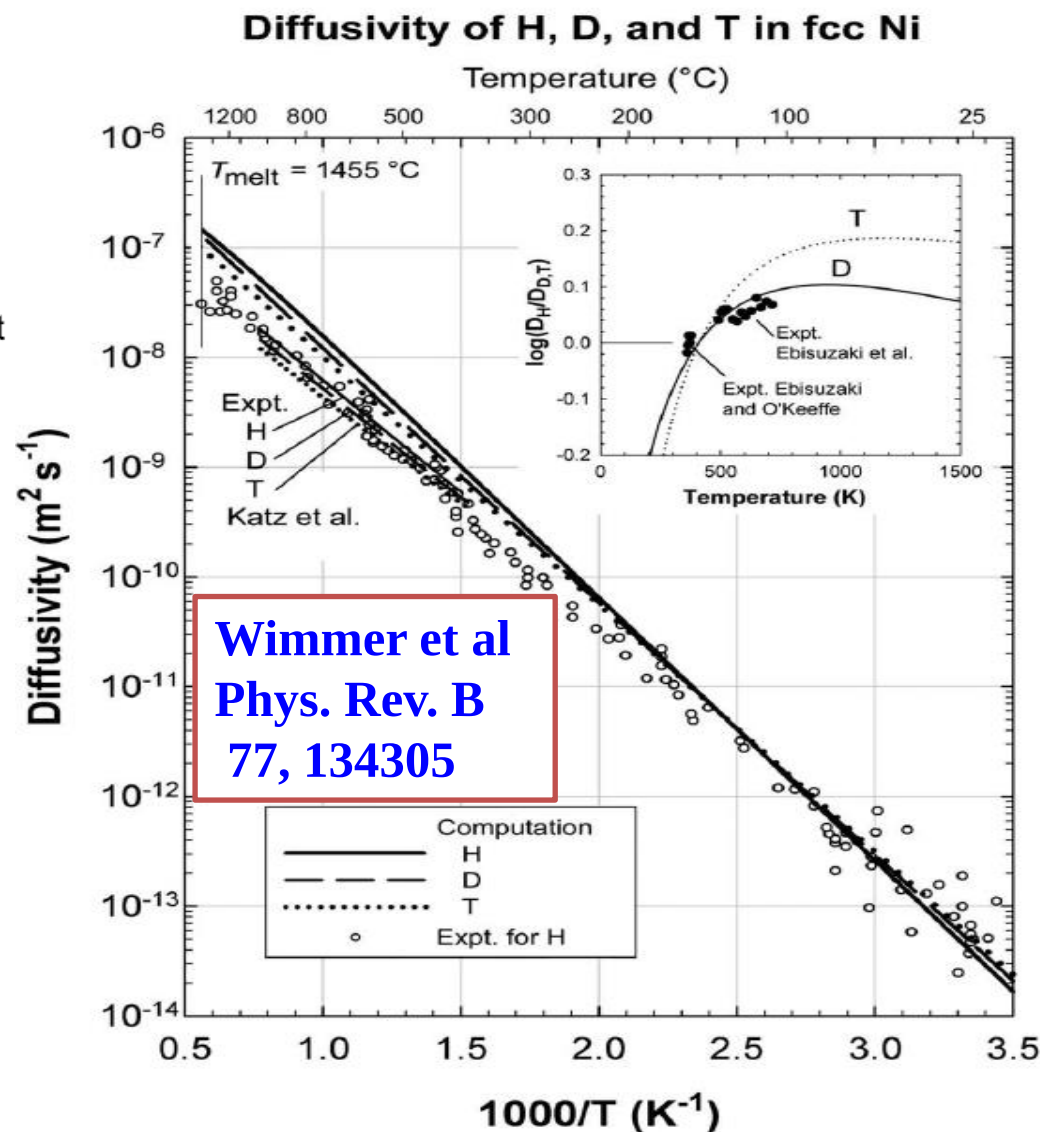
At present, it is very hard to give a reliable value for the solubility and diffusivity in tungsten, and data for this is urgently required.

First-principles computational methods →→ solubility and diffusivity

First-principles computational methods are now possible to calculate the solubility and diffusivity of foreign interstitial atom in metals at a level of accuracy close to and sometimes better than available from experiments.



Chen Ling et al Phys. Rev. B 80, 214202



First-principles computational data of H diffusivity in tungsten

Heinola et al J. Appl. Phys. 107 113531

Unfortunately, the calculated diffusivities show large differences from the experimental values, particularly at low temperatures, suggesting that some important factors might have been missed in these two first-principles calculations

The temperature effect may be one such omission, as this has been demonstrated to be an important actor for an accurate interpretation of experimental solution and diffusion data using first-principles computational methods.

The defect-trapping effect may also contribute to the large difference of the reported hydrogen solubility and diffusivity data, which has been found to significantly affect the hydrogen solution and diffusion behaviors in metals, particularly at low temperatures.

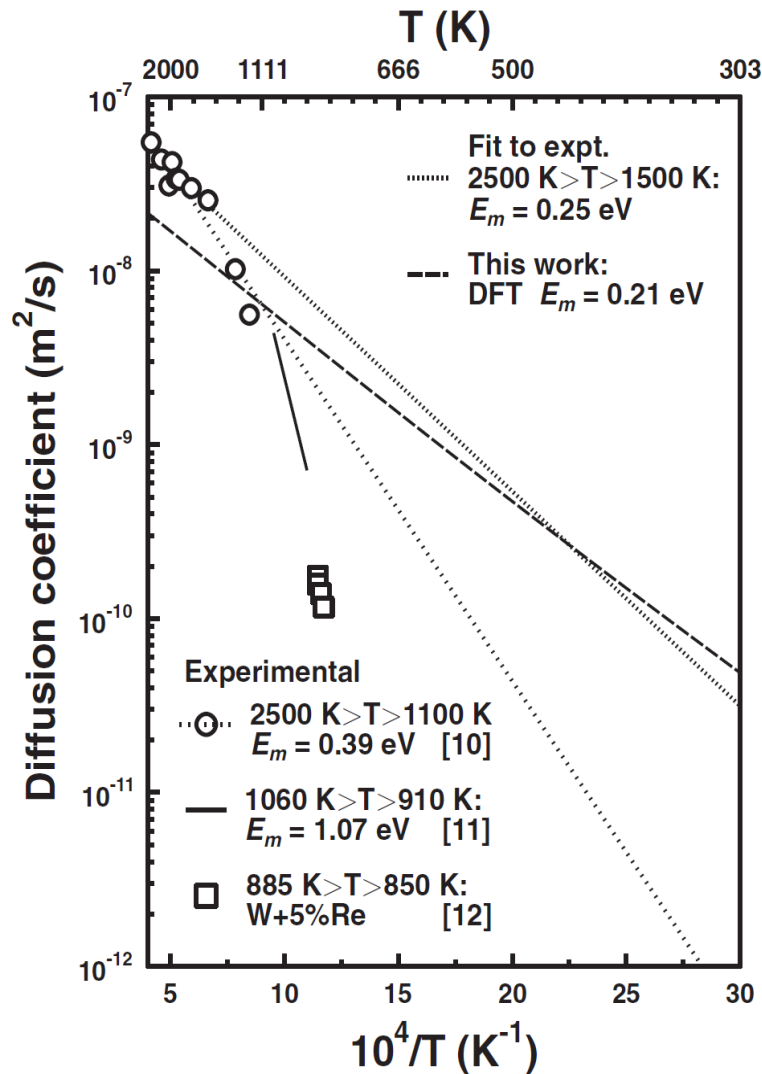


FIG. 4. Calculated hydrogen diffusion coefficient D compared to the experimental values. The trapping effect gets pronounced at temperatures below 1100 K, where the experimental D values fall under the extrapolated Arrhenius fit of the Frauenfelder data (Ref. 10) (dotted line with wide spacing). Omitting the two lowest experimental points in Frauenfelder data, decreases the migration barrier from 0.39 to 0.25 eV.

We carry out a systematic first-principles calculation to investigate the dissolution and diffusion properties of interstitial hydrogen in tungsten.

Solution energy

$$E_{\zeta}^{Sol} = E^{WH_{\zeta}} - (E^W + E^H)$$

Total energy of the W system with a singel H atom in ζ site

Total energy of perfect W system.

Energy of a singel H aotm, half the energy of a H molecule.

Solubility

$$S_{\zeta} = \frac{\sqrt{P}}{\sqrt{P_0}} \exp\left(\frac{\Delta ST - E_{\zeta}^{Sol}}{kT}\right)$$

Here, P and P_0 are the background pressure and the reference pressure (we choose standard pressure in order to make a comparison with the experiment), respectively, k is the Boltzmann constant and T is the temperature. ΔS is the entropy of solution, equal to about $-4.7k$ [43], which is almost negligible.

Activation energy

$$E_{act} = E^{TS} - E^{IS}$$

Jump rate (WZ)

$$\Gamma = n \sqrt{\frac{E_{act}}{2m\lambda^2}} \exp\left(\frac{-E_{act}}{kT}\right)$$

Jump rate (hTST)

$$\Gamma = n \frac{kT}{h} \frac{\prod_{i=1}^{3N-1} \frac{\exp(\frac{-h\nu_i^\ddagger}{2kT})}{1 - \exp(\frac{-h\nu_i^\ddagger}{kT})}}{\prod_{i=1}^{3N} \frac{\exp(\frac{-h\nu_i}{2kT})}{1 - \exp(\frac{-h\nu_i}{kT})}} \exp\left(\frac{-E_{act}}{kT}\right)$$



Diffusivity

$$D = \frac{1}{6} \lambda^2 \Gamma$$

n : the number of the nearest-neighbor interstitial positions,

m : the mass of a hydrogen atom.

E_{act} : the activation energy, defined as the difference in the minimum energy of the transition state (E^{TS}) and of the initial state (E^{IS})

Temperature effects

Xiao-Gang Lu, Comput. Coupling Phase Diagrams Thermochem. 2005;29:68

Thermal expansion

$$a_T = a_0 \frac{a_T^{Lu}}{a_0^{Lu}}$$

$$V_T = V_0 \exp\left(\int_{T_0}^T 3\alpha dT\right)$$

$$\alpha = a + bT + cT^2 + dT^{-2}$$

The lattice constants of Lu (a_T^{Lu}) cannot be directly used to interpret our density functional theory (DFT) calculations because of the small difference between the DFT optimized lattice constant at 0 K (a_0) and the experimental observation.

Element	Stable structure	$V_0, 10^{-6} \text{ m}^3/\text{mol}$	Parameters			
			$a, 10^{-5} \text{ K}^{-1}$	$b, 10^{-8} \text{ K}^{-2}$	$c, 10^{-11} \text{ K}^{-3}$	d, K
W	bcc	9.50328	1.36240	—	0.14796	−0.055762

Free energy

$$F^A(T) = E_c^A(a_T) + F_\nu^A(a_T)$$

Static energy

Vibrational free energy

$$F_\nu^A(a_T) = \sum_i h\nu_i^A(a_T)/2$$

$$+ k_B T \ln(1 - \exp(-h\nu_i^A(a_T)/kT))$$

The temperature effect is taken into account by the thermal expansion and vibration free-energy contribution.

Trapping effects

**Effective
diffusivity**

$$D_{eff} = \frac{D_{perf}}{1 + c_{trap} \exp\left(\frac{E_{trap}}{kT}\right)}$$

D_{perf} is the diffusivity at the perfect system without traps

c_{trap} is the trap concentration

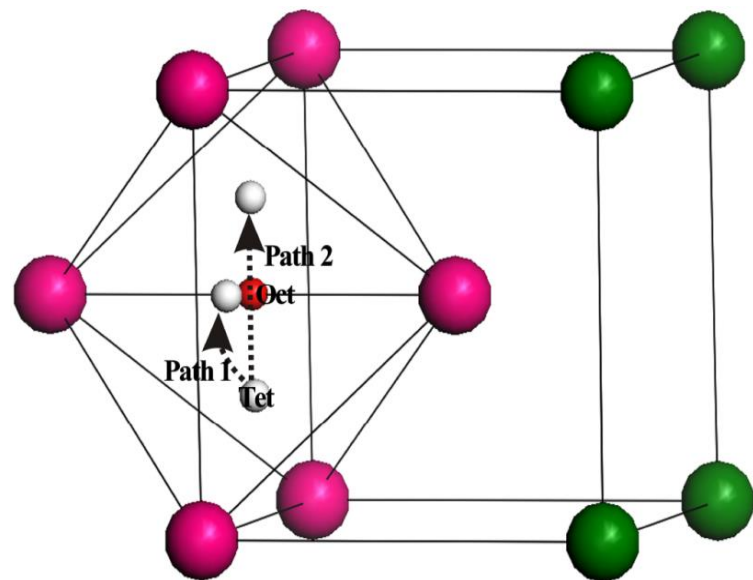
E_{trap} is the trapping energy of hydrogen in the trap site

The defect-trapping effect is described through the classic Mac-Nabb and Foster formula ([Oriani, Acta Metall. 18, 147\(1970\)](#)).

Table 1. The relevant lattice constant (a_T) and their corresponding lattice expansion ratios ($\Delta a_T/a_0$).

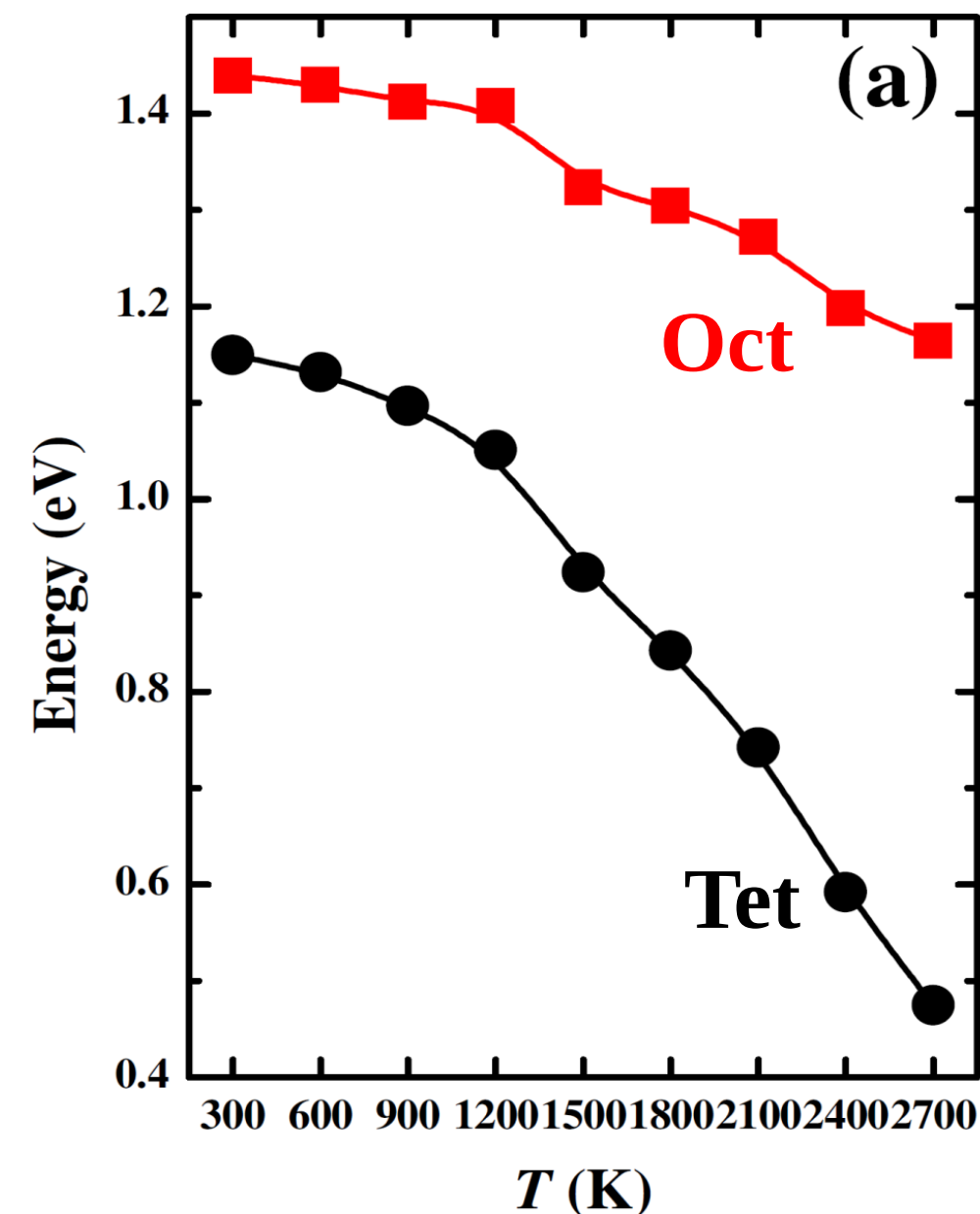
Temperature (K)	a_T (Å)	$\Delta a_T/a_0$ (%)
0	3.177	0.000
300	3.180	0.096
600	3.184	0.235
900	3.189	0.378
1200	3.193	0.526
1500	3.198	0.684
1800	3.204	0.855
2100	3.210	1.043
2400	3.216	1.248
2700	3.223	1.474

Table 2. Comparison of properties of hydrogen solution and diffusion in tungsten at 0 K as obtained by DFT calculations: E_{Tet}^{Sol} is the solution energy of hydrogen at the ground state, i.e. tetrahedral interstitial site, $\Delta E_{Oct-Tet}^{Sol}$ is the energy difference between the octahedral and tetrahedral solution sites, E_{act} is the activation energy of hydrogen jumping between two adjacent tetrahedral interstitial sites, ν_{GS} and ν_{TS} are the vibration frequencies at the ground state and at the transition state, respectively.



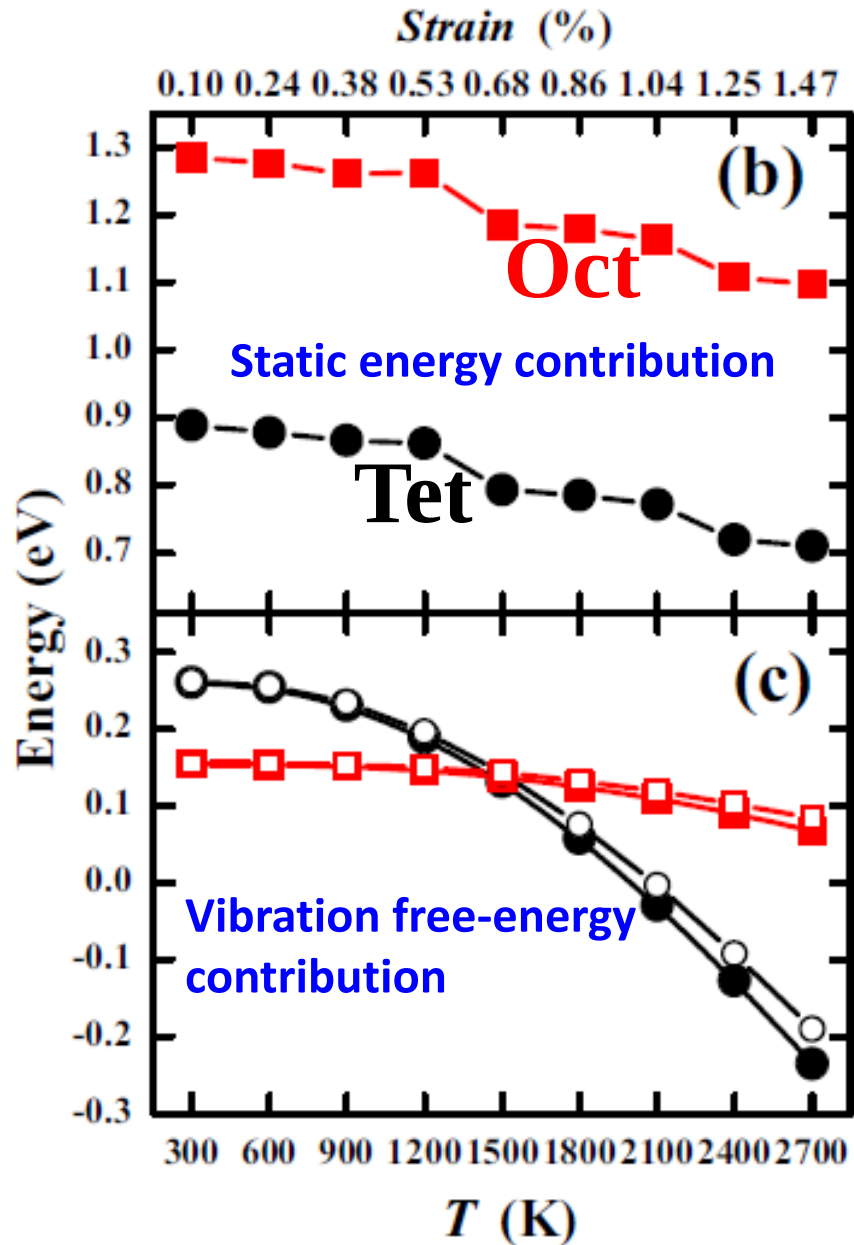
	other	This work
E_{Tet}^{Sol} (eV)	0.90 ^a , 0.92 ^b , 0.95 ^c	0.89
$\Delta E_{Sol}^{Oct-Tet}$ (eV)	0.40 ^a , 0.38 ^c	0.40
E_{act} (eV)	0.21 ^c	0.22
ν_{GS} (THz)	46.7 ^c , 46.7 ^c , 34.7 ^c	46.0, 46.0, 34.4
ν_{TS} (THz)	63.3 ^c , 45.6 ^c , 24.9 ^c	62.3, 46.3, 25.8

- ◆ Hydrogen atom prefers to occupy the tetrahedral (Tet) interstitial site rather than the octahedral (Oct) interstitial site.
- ◆ Our calculated results are in good agreement with the former theoretical data.



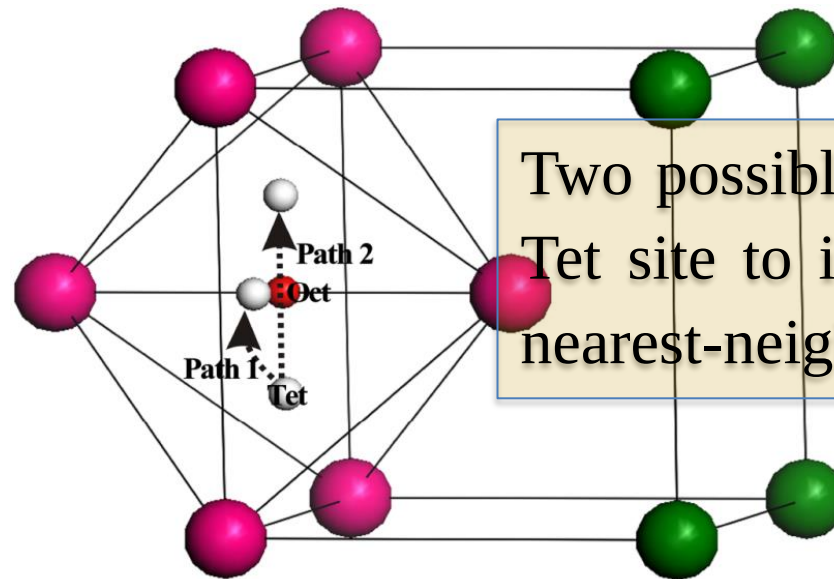
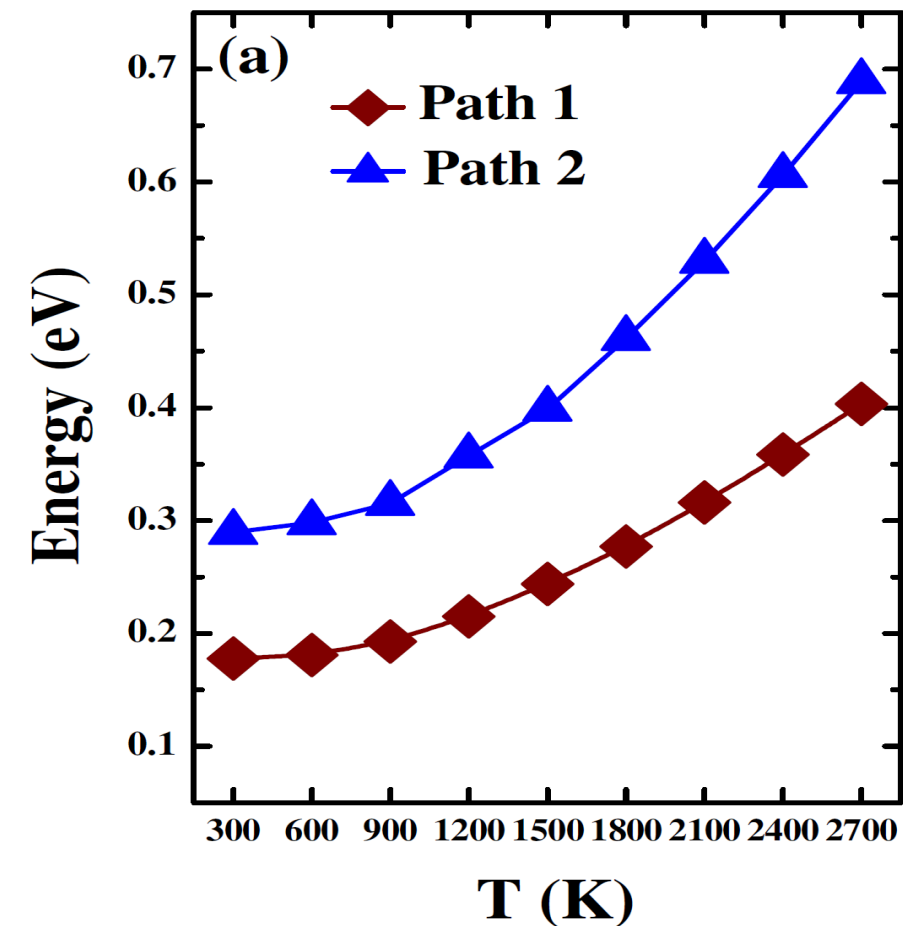
- The interstitial hydrogen atom always **prefers to occupy the Tet site** rather than the Oct site over the temperature range .
- The solution energy in both Tet and Oct geometry decreases with temperature, suggesting **the dissolution of hydrogen becomes easier** with the temperature increase.
- It decreases faster in the Tet geometry than in the Oct geometry, meaning **the stabilization is much more significant for the Tet site** than the Oct site when the temperature increase.

The temperature dependent **solution energy**.



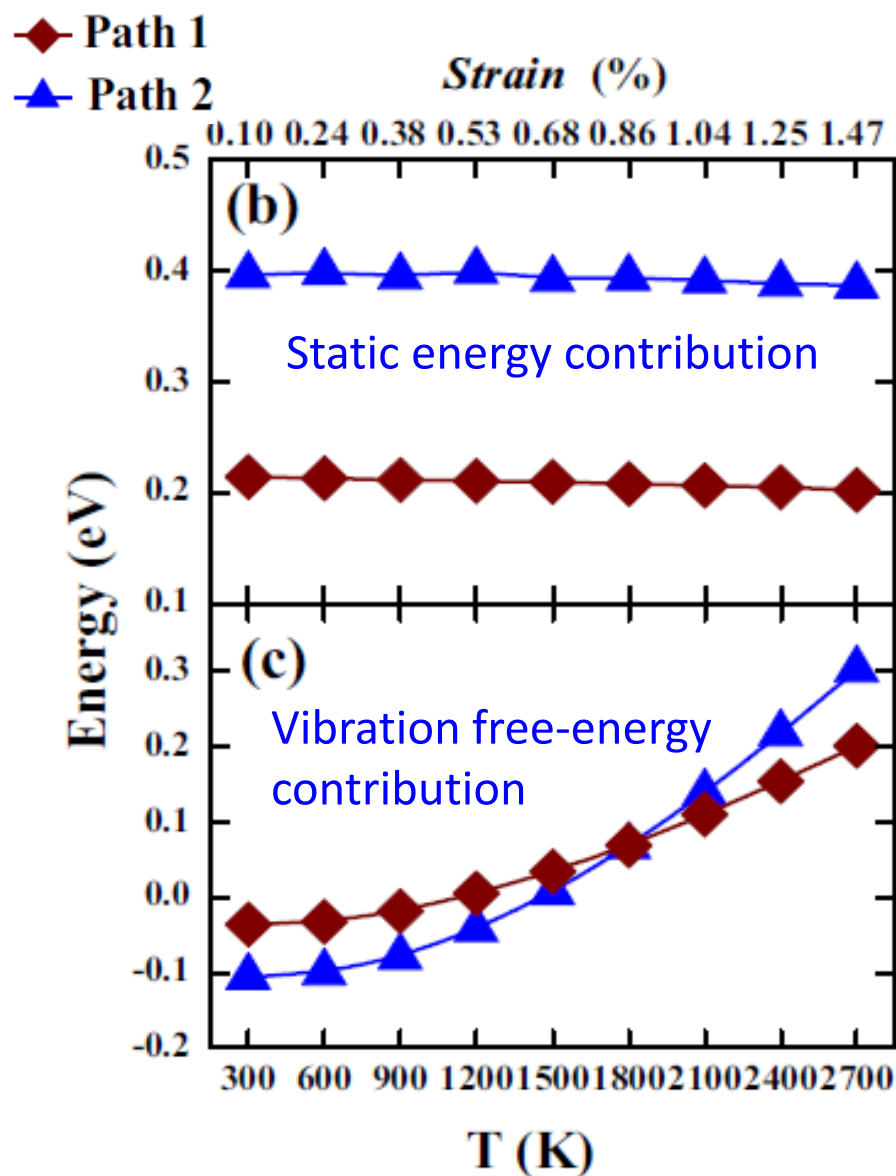
- The static energy contribution shows a linear-like negative temperature dependence, and the value decreases about 0.20 eV from 300 to 2700 K .
- The vibration free-energy contribution decreases with the temperature exponentially .

The temperature dependent **solution energy**.



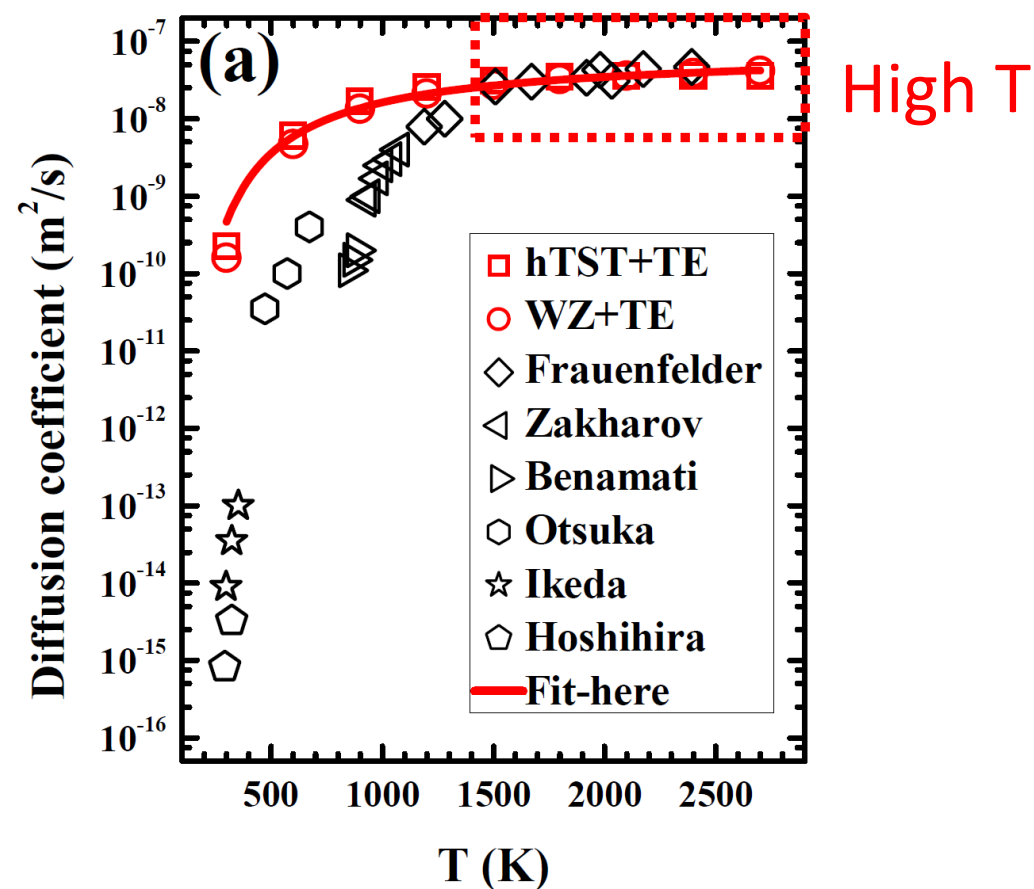
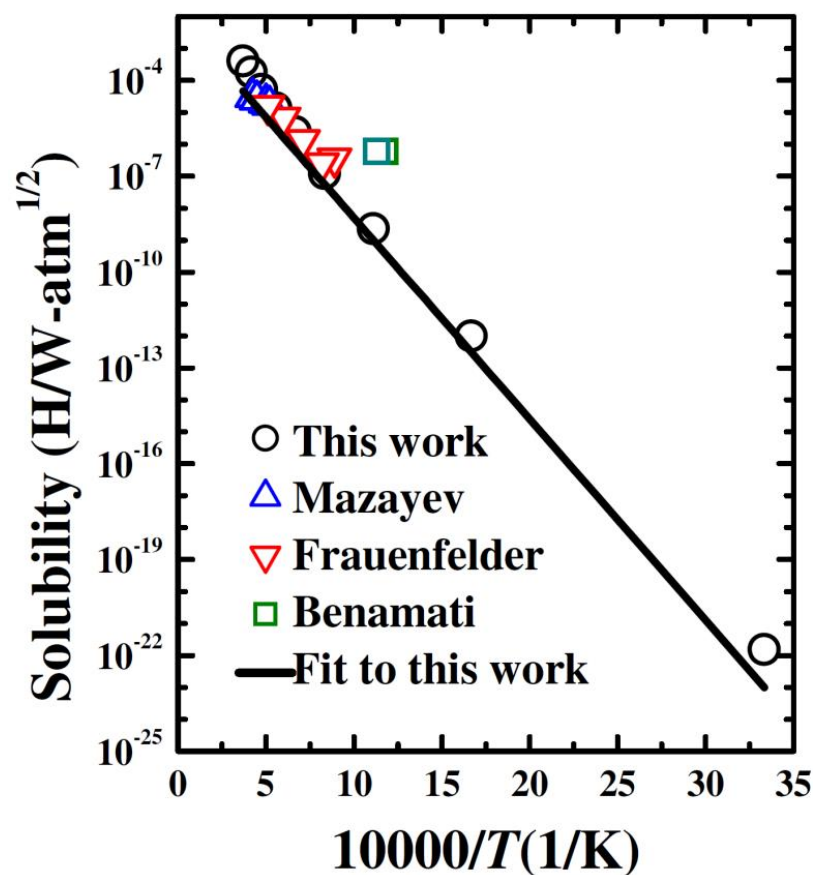
- The activation energies increase with the temperature, implying much more energy are needed for hydrogen hopping between two adjacent Tet sites at high temperature.

- The activation energy of Path 1 is always less than that of Path 2, and the difference between them becomes larger as the temperature increase. Hence, it can be deduced that **the migration path of interstitial hydrogen mainly advances via the nearest neighboring Tet sites in tungsten.**



- The static energy contribution are always about 0.2 and 0.4 eV for Path 1 and 2, almost independent of the temperature.
- The vibration free-energy contribution plays a dominant role in the behavior of the activation energy with temperature.

The temperature dependent **activation energy**.

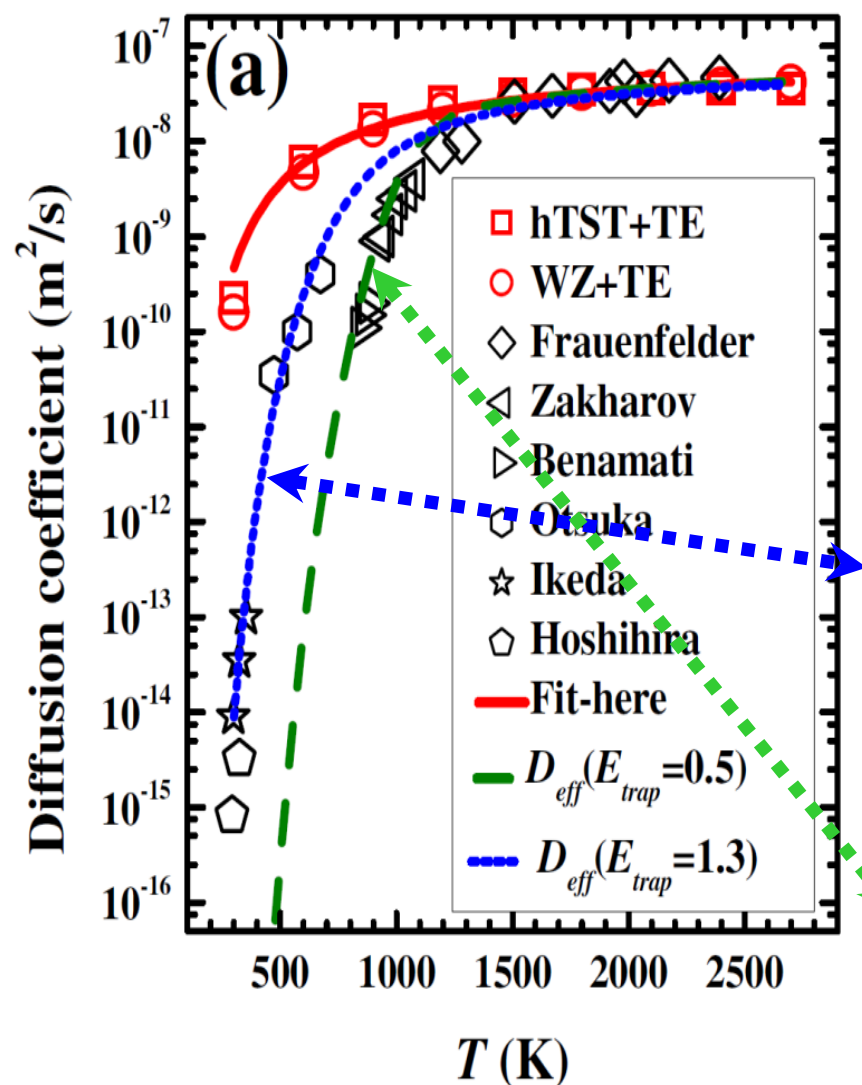


- Our predicted hydrogen solubility and diffusivity are in very good agreement with the experimental data **above ~1500 K**, but smaller and higher than their corresponding experimental values below 1500K, respectively.
- The significant deviation below 1500 K can be explained by the **trapping phenomenon**.

Two type typical defect-trapping effect:

Natural traps (impurity, dislocation, GB): 0.5 eV; concentration: 10^{-2} and lower.

Vacancies: 1.3 eV, concentration: 10^{-6} and lower.



$$D_{eff} = \frac{D_{perf}}{1 + c_{trap} \exp\left(\frac{E_{trap}}{kT}\right)}$$

The predicted effective diffusivity in field of **natural traps** shows consistency with the experimental values at the temperature of **300-600K**.

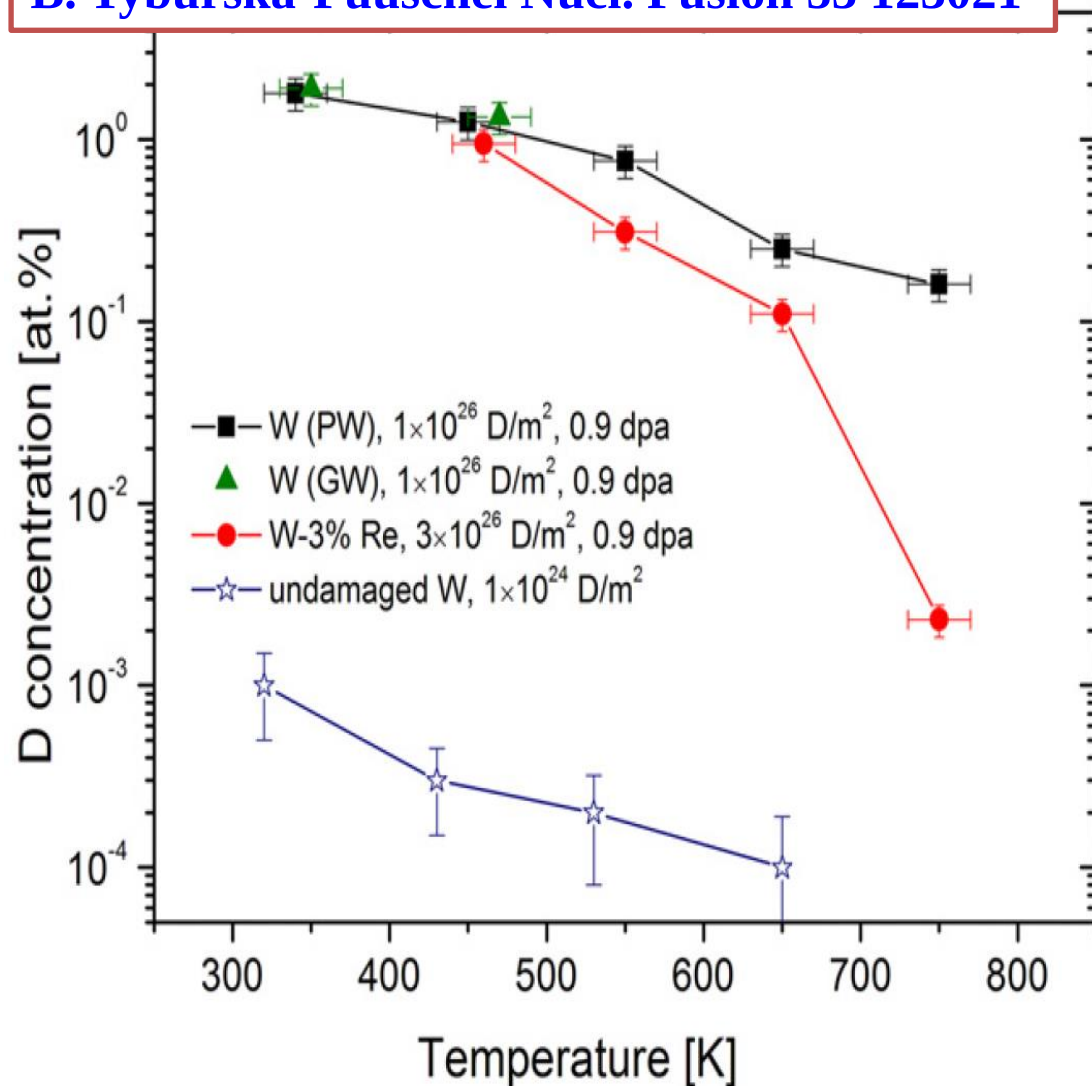
The predicted effective diffusivity in field of **vacancies** is in agreement with the experimental values at the temperature range of **800-1200K**.

-
1. Our results reveal that both solution and activation energies are strongly temperature-dependent.
 2. The predicted solubility and diffusivity show good agreement with the experimental data above 1500 K, but present a large difference below 1500 K, which can be bridged by the trapping effects of vacancies and natural trap sites.
 3. The present study reveals a dramatic effect of temperature and trapping on the hydrogen solution and diffusion properties in tungsten, and provides a sound explanation for the large scatter in the reported values of hydrogen diffusivity in tungsten.
 4. Generally, the alteration of the diffusivity resulted from the decrease or increase in the activation energy is moderated by the variation of the pre-exponential factor.

First-principles calculations of transition-metal solute interactions with point defect and hydrogen in tungsten.

In order to evaluate energetically the transitional metal (TM) solute role in modifying the hydrogen retention behavior.

B. Tyburska-Püschel Nucl. Fusion 53 123021

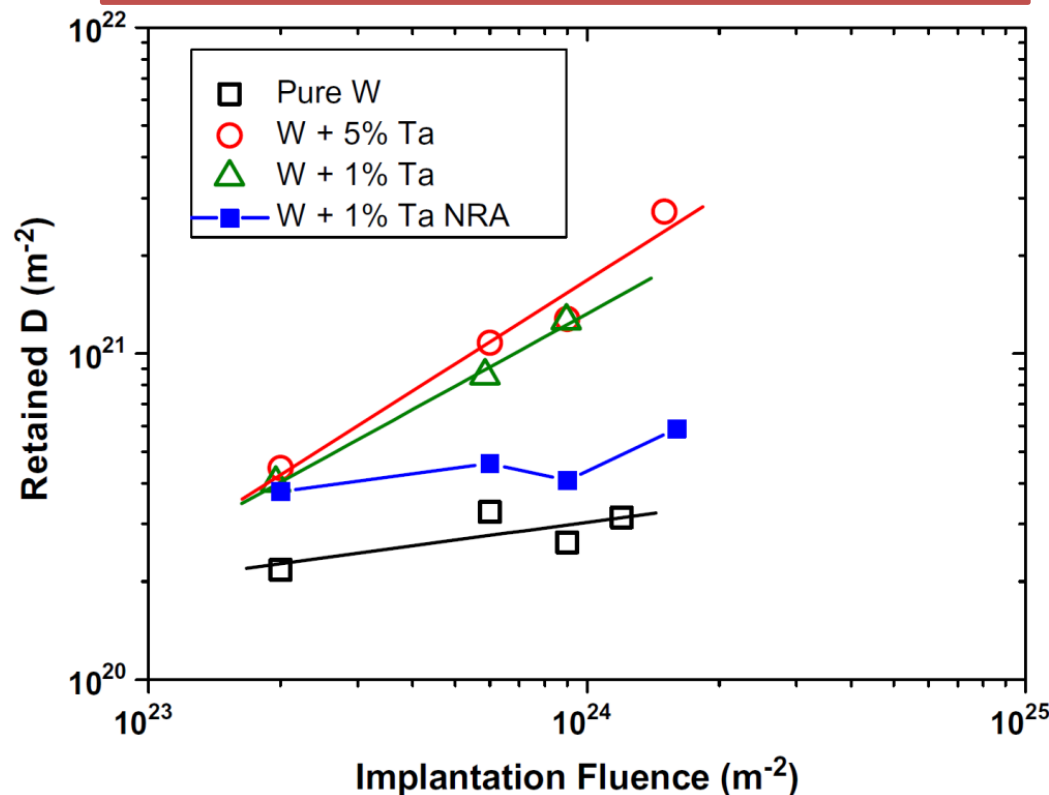


- Adding Re into W material leads to a decrease in the D concentration at exposure temperatures above 450K.
- It can drop significantly faster in W-Re than in pure W, given sufficiently high temperatures.

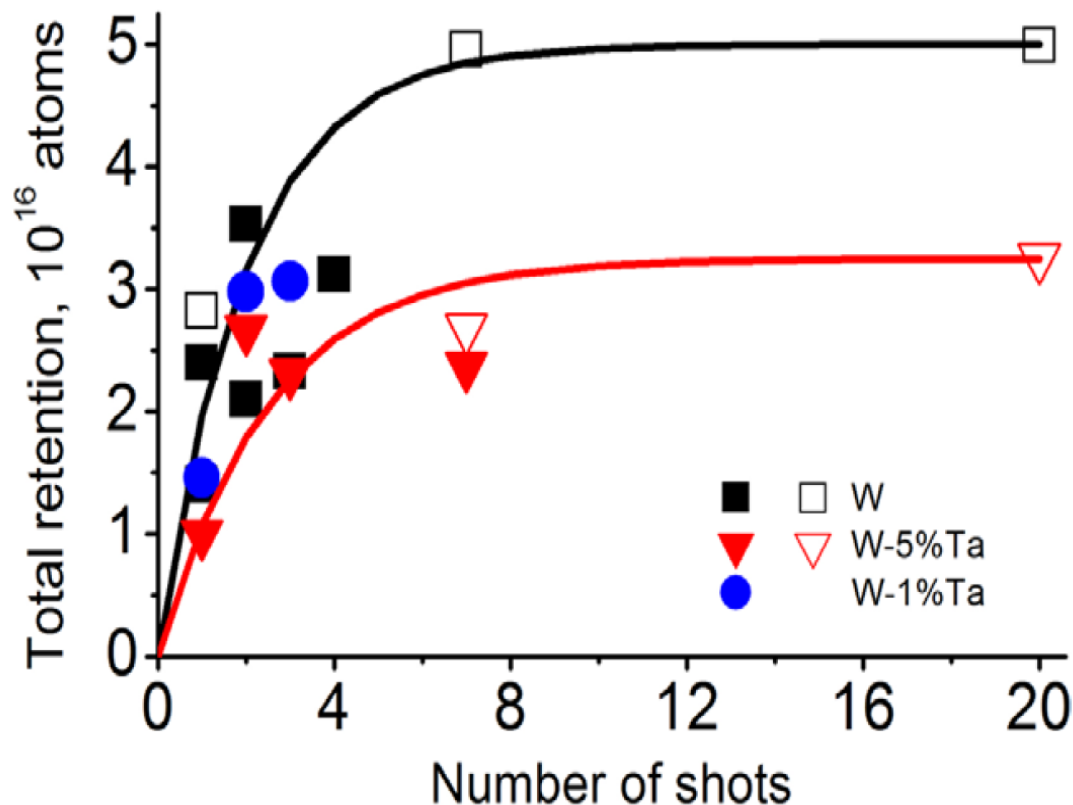
Similar changes in retention behavior were **not observed** in **undamaged samples**.

Why ?

K. Schmid J. Nucl. Mater. 426(2012)247



Y. Zayachuk Nucl. Fusion 53 (2013)013013



Ion fluxes $\sim 10^{19} \text{ m}^{-2} \text{ s}^{-1}$

$\sim 8 \times 10^{23} - 10^{24} \text{ m}^{-2} \text{ s}^{-1}$

In the **low fluxes** conditions, the deuterium retention in W-Ta was significantly **higher** than in W.

Why?

In the **high fluxes** conditions, deuterium retention was systematically **lower** in W-Ta than in W

Explanation by Y. Zayachuk in Nucl. Fusion 53 (2013)013013

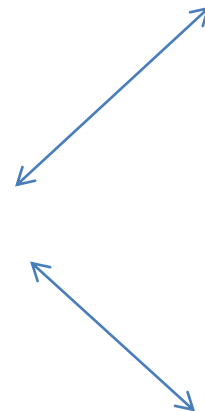
1. Retention at low flux was most probably dominated by trapping on **pre-existing defects**.
2. For high ion flux conditions, deuterium retention is strongly influenced by the **plasma induced material modification**. This modification rather than the initial difference in the microstructure predominantly determines the difference in retention between W and W-Ta.

The interactions between

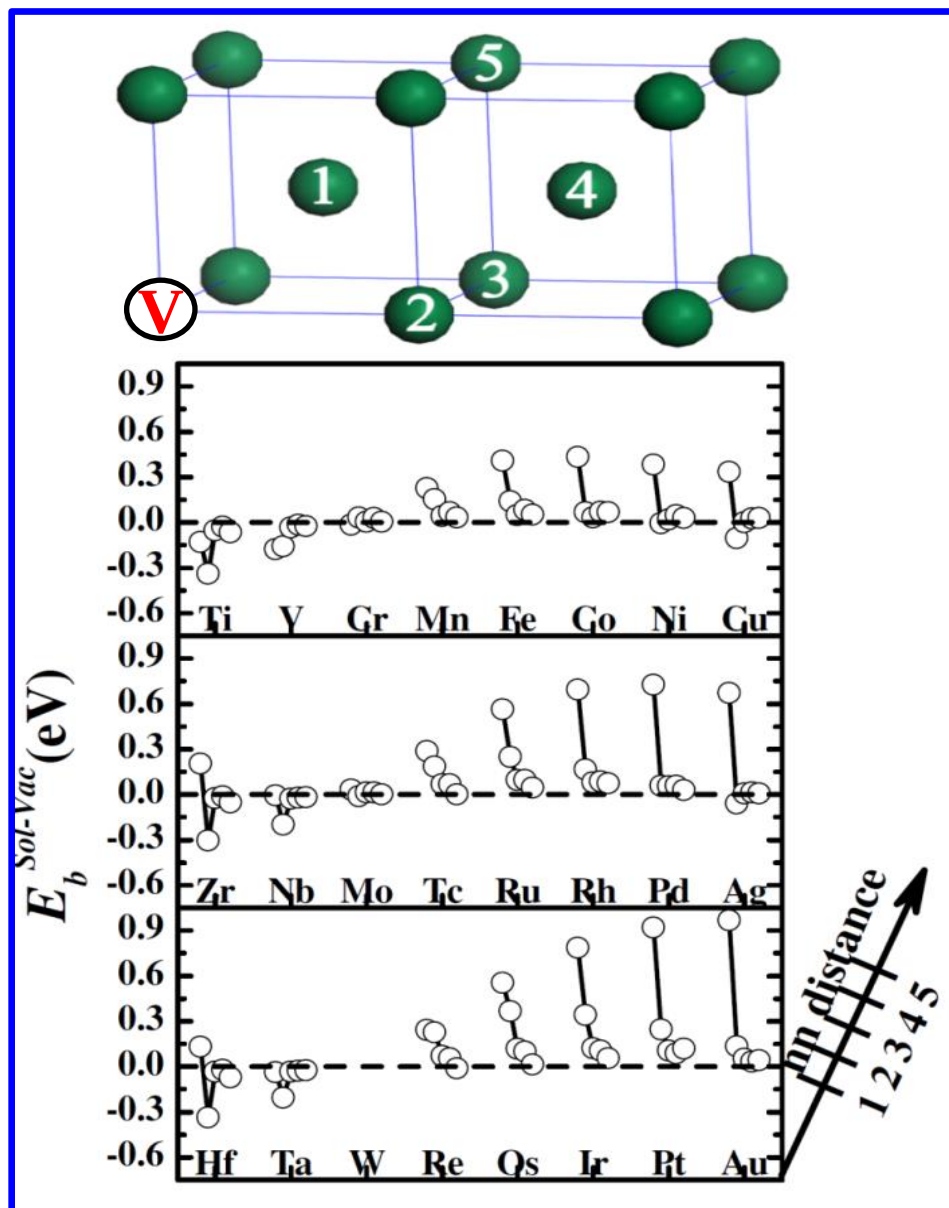
Solute

SIA and V

Hydrogen



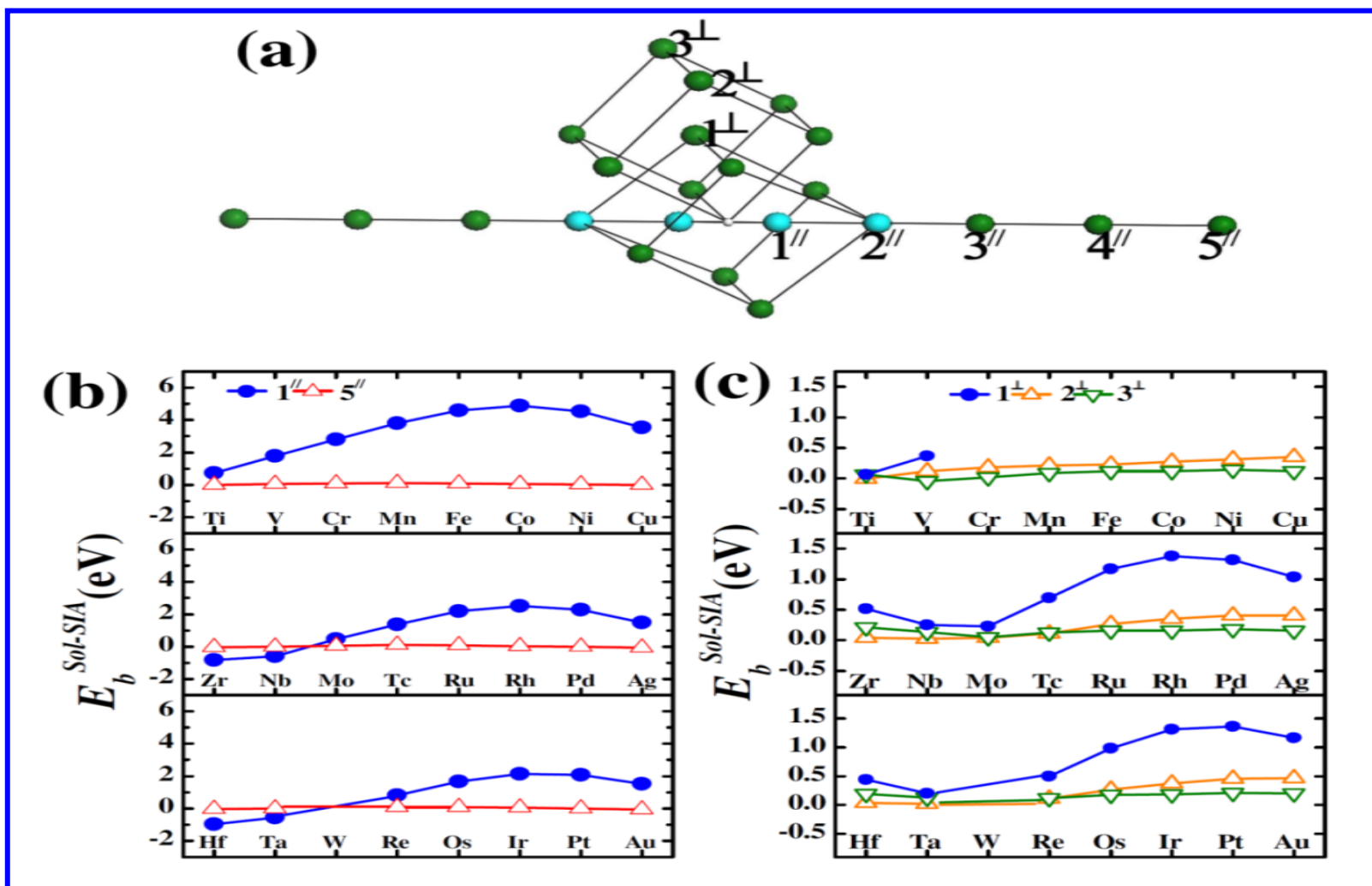
Results: The interaction of TM solute with vacancy



- The solute–vacancy interaction is very **local**, limited to within the second nearest-neighbor shell.
- The binding energy in the range of -0.3~0.6 eV
- The interaction are mostly **attractive** with a few exceptions

Solute–vacancy binding energies of TM elements in W

Results: The interaction of TM solute with self-interstitial atom



- The interaction range is an **ellipsoid around the center of the $\langle 111 \rangle$ -crowdion** with the semi-major axis 11 Å in $\langle 111 \rangle$ -crowdion direction and semi-minor axis 3 Å
- The interaction are mostly **attractive** with a few exceptions, which is much stronger in the major axis than that in the minor axis

Results: The interaction of TM solute with vacancy and self-interstitial atom

Solute-SIA attractive interaction

>

Solute-V attractive interaction

SIAs are slowed down



Closes the gap in the mobility bias between SIA and V



Increase recombination



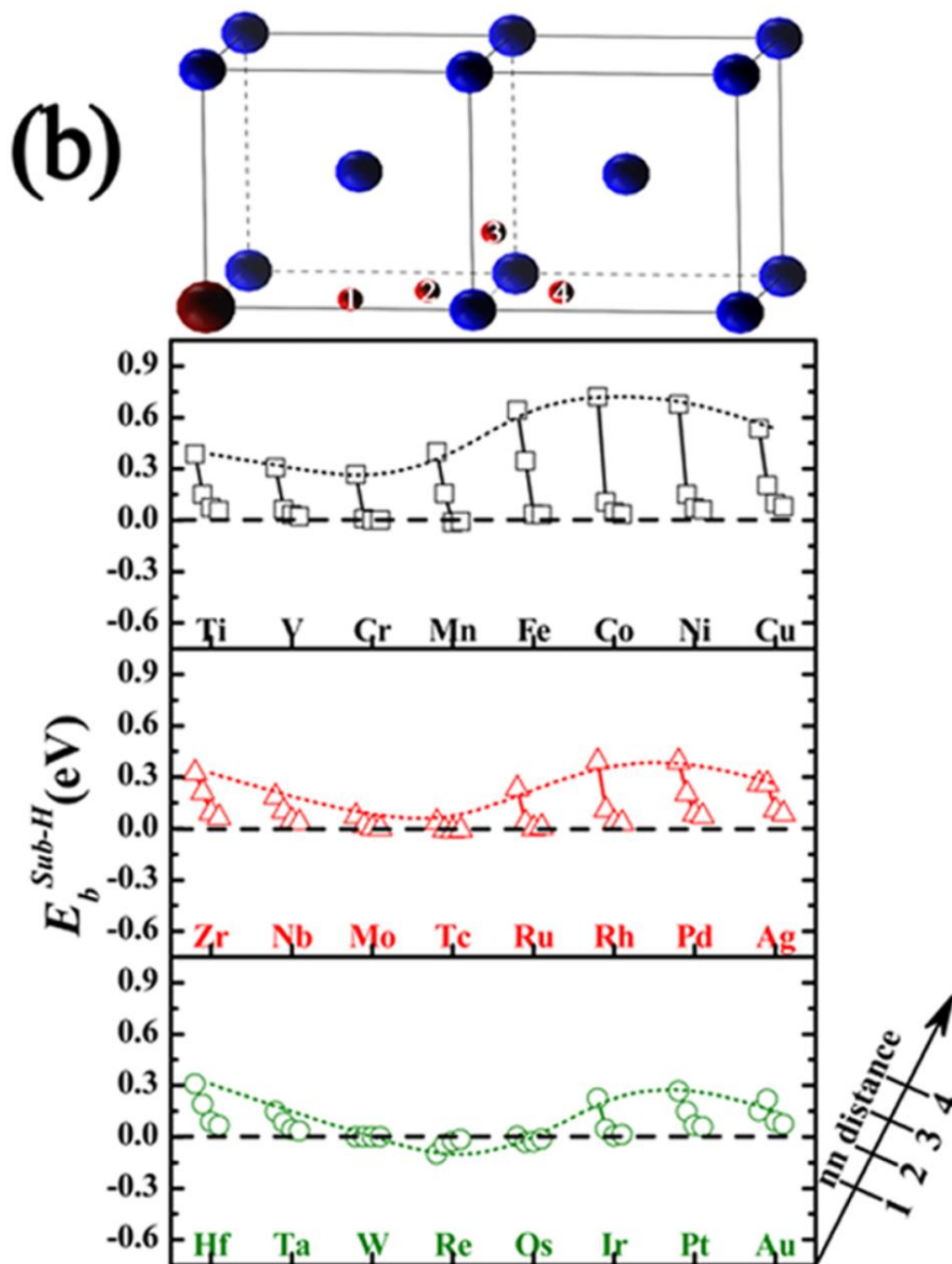
Decreased the defect concentration



Decrease the hydrogen retention

The sequence of the solute effect:

$\text{Os} > \text{Re} > \text{Ta} \gg \text{V} > \text{Hf} > \text{Ti}$



➤ the solute-H interaction is very local, limited within the second nearest-neighbor shell.

➤ Most of the solute-H binding energies are positive, suggesting an attractive interaction between the solute atom and hydrogen.

The exceptions are Re-H and Os-H with a repulsive interaction.

Results: The effects of TM solutes on the hydrogen distribution

Simonovic model (PRB 81 054116)

SSA: substitutional solute atoms

ISA: interstitial solute atoms (H)

The probability of ISA is present at the i th nearest neighboring cell of the SSA

$$f_{inn} = f_{\infty} \exp[E_b^{SSA-ISA}(inn)/(k_B T)]$$

the fraction of the interstitial sites filled with ISA where the SSA has no influence on the ISA.

the binding energy of the SSA with ISA at its i th nearest-neighboring shells

f_{∞}

The ISA concentration (10^{-3})

$$C_{ISA} = C_{SSA} \sum_{i=1}^{max} n_i f_{inn} + (N_{int} - C_{SSA} \sum_{i=1}^{max} n_i)$$

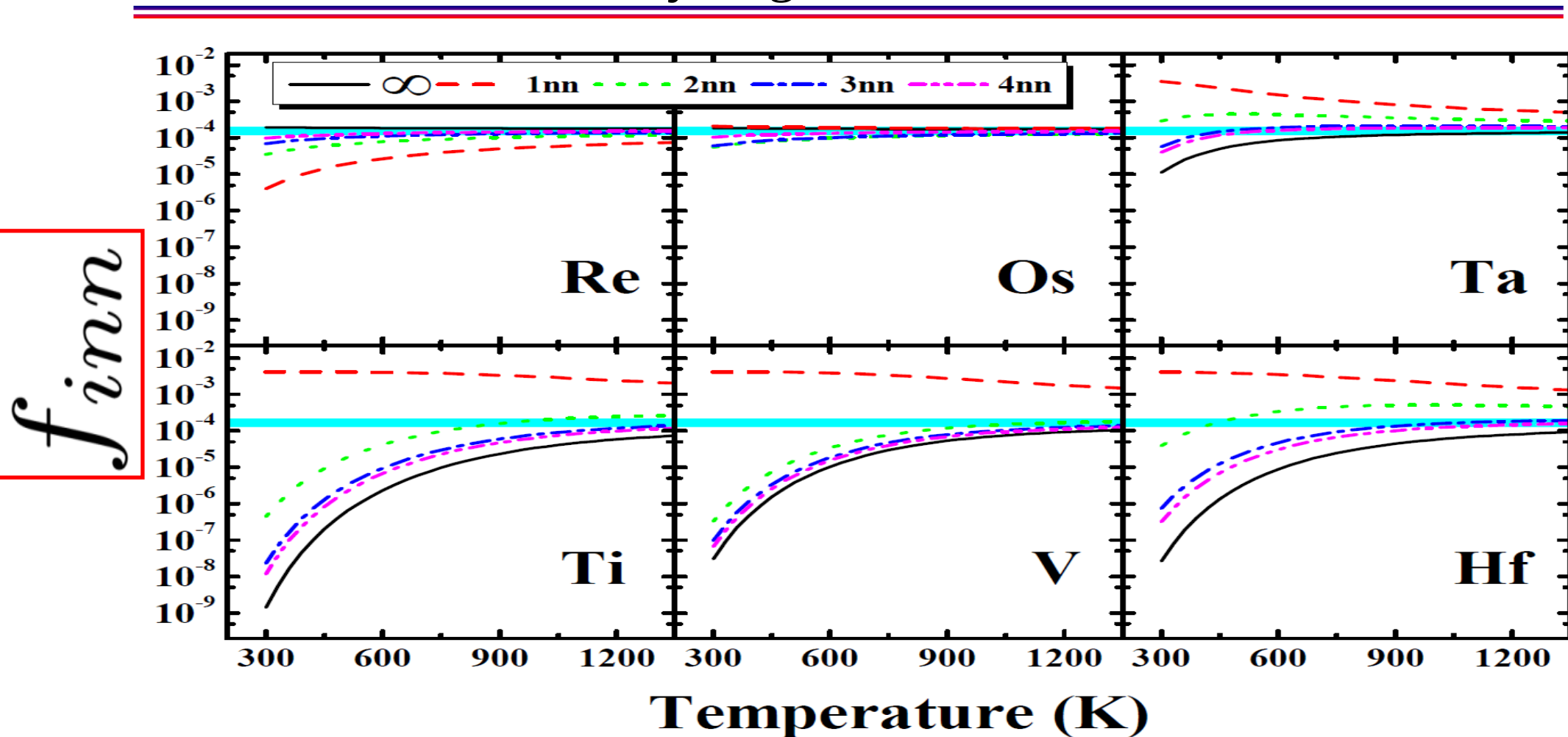
The SSA oncentration (10^{-2})

The number of the interstitial sites per atom in the lattice (6)

The number of the interstitial sites in the inn cell

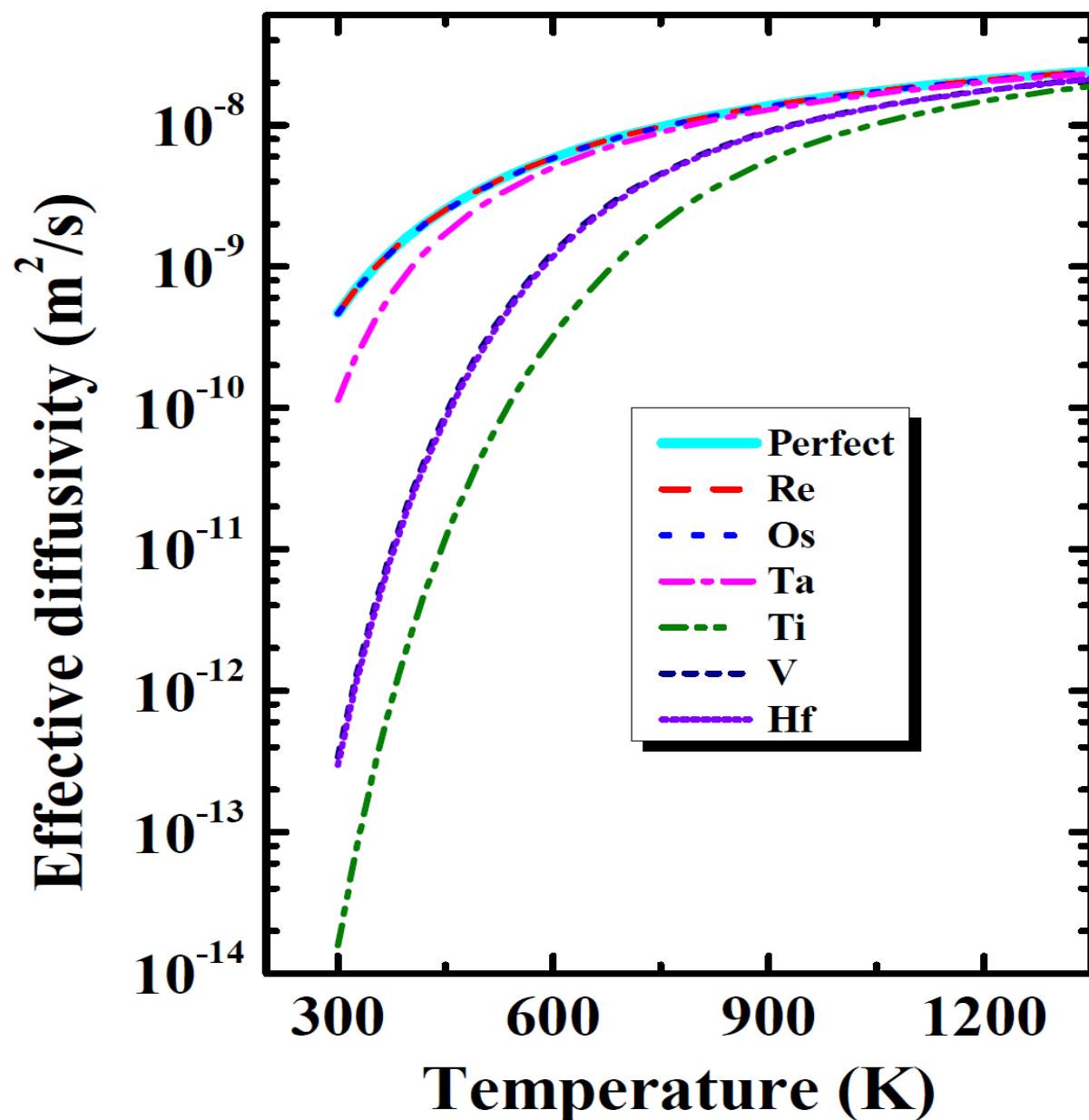
f_{inn}

Results: The effects of TM solutes on the hydrogen distribution



- Re and Os have little effect on the hydrogen distribution while the segregation of hydrogen around Ta, Ti, V, and Hf increases the solubility of hydrogen in W.
- The influence of Ta, Ti, V, and Hf on the hydrogen solubility in tungsten is step-down with increasing temperature.

Results: The effects of TM solutes on the hydrogen diffusion



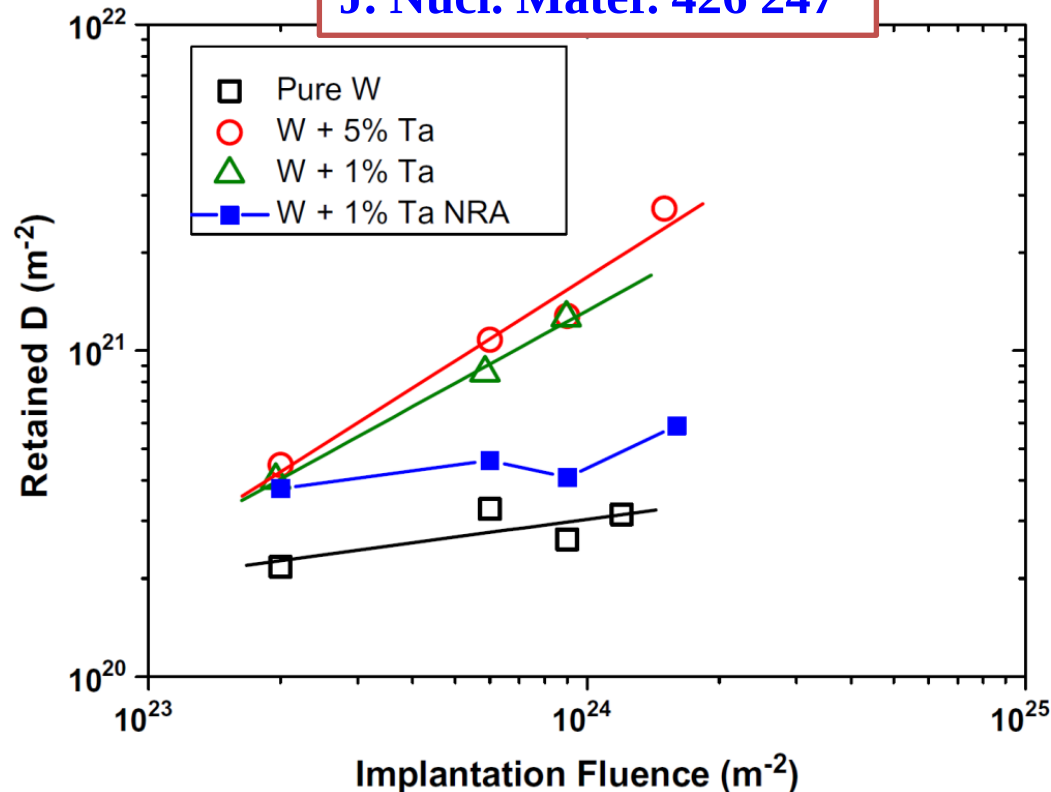
$$D_{eff} = \frac{D_{perf}}{1 + \frac{N_{Sol}}{N_W} \exp\left(\frac{E_b^{Sol-H}}{kT}\right)}$$

Re and Os exert little effect on the hydrogen effective diffusivity,

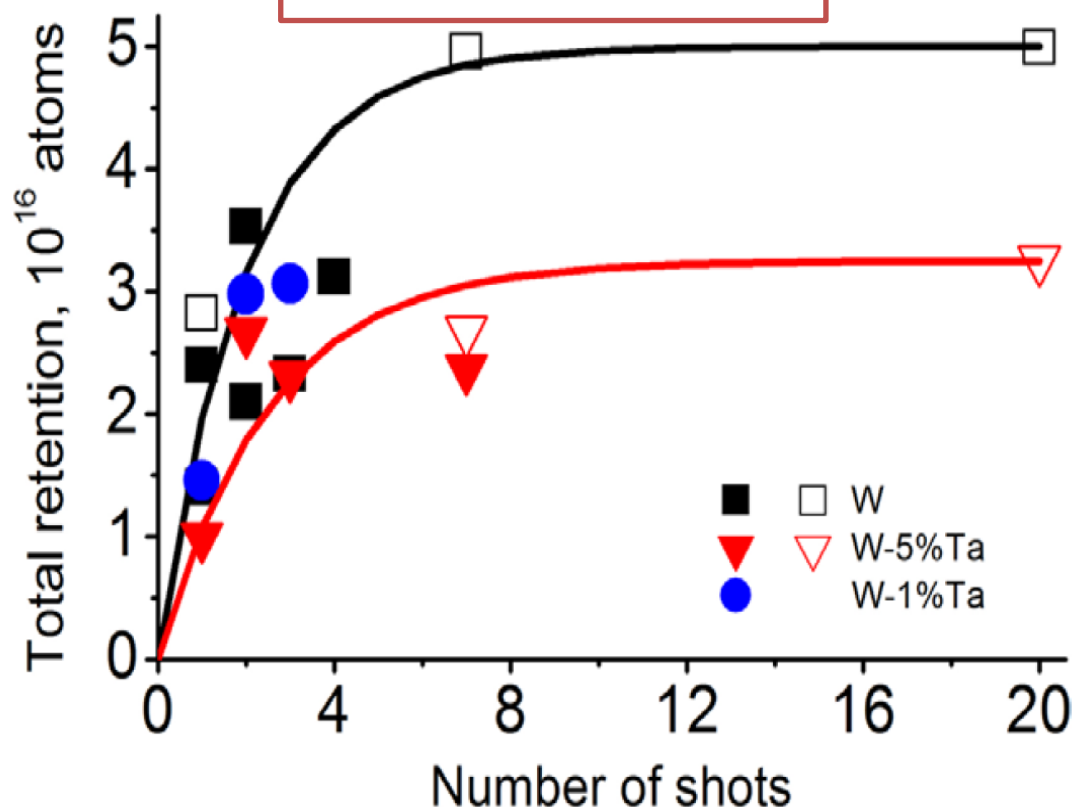
and Ta slightly decreases the hydrogen effective diffusivity,

while Ti, V, Hf significantly reduce the hydrogen effective diffusivity.

J. Nucl. Mater. 426 247



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fluence $2.3 \times 10^{23} - 1.2 \times 10^{24} \text{ m}^{-2}$

$3.5 \times 10^{26} - 10^{27} \text{ m}^{-2}$

Retention at low flux was most probably dominated by trapping on pre-existing defects.

No solute effect.

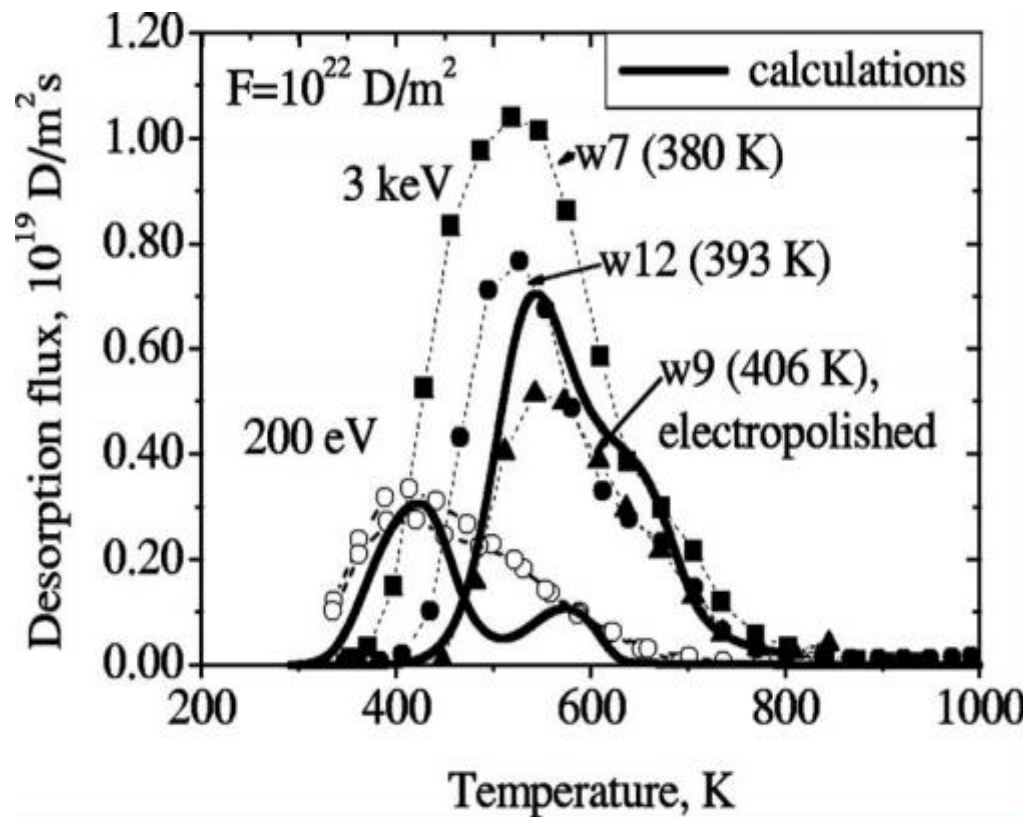
Deuterium retention is strongly influenced by the radiation-induced defects. **Solute Ta decreases defect concentration**

-
- The interaction of TM with point defect are mostly attractive with a few exceptions, which are significantly weaker with vacancy than with the SIA. It can be expected that interstitials are slowed down, closes the gap in the mobility bias between interstitial and vacancy type clusters and increase the recombination of the vacancy with interstitial, ultimately reduce the retention of hydrogen in W
 - The attractive interaction between the TM solute atom and hydrogen suggest that TM solutes can trap multiple hydrogen atoms in their neighbor shells to form many small hydrogen clusters and decrease the hydrogen effective diffusivity, which could, to some extent, prevent the occurrence of large bubbles, but may significantly increase the hydrogen retention in tungsten.
 - The combination of these findings could provide a good explanation for recent experimental results.

Ongoing work:
**Multi-scale modeling on the hydrogen
retention and desorption in tungsten**

In order to interpret the experiment results (thermal desorption spectrum) with atomic level.

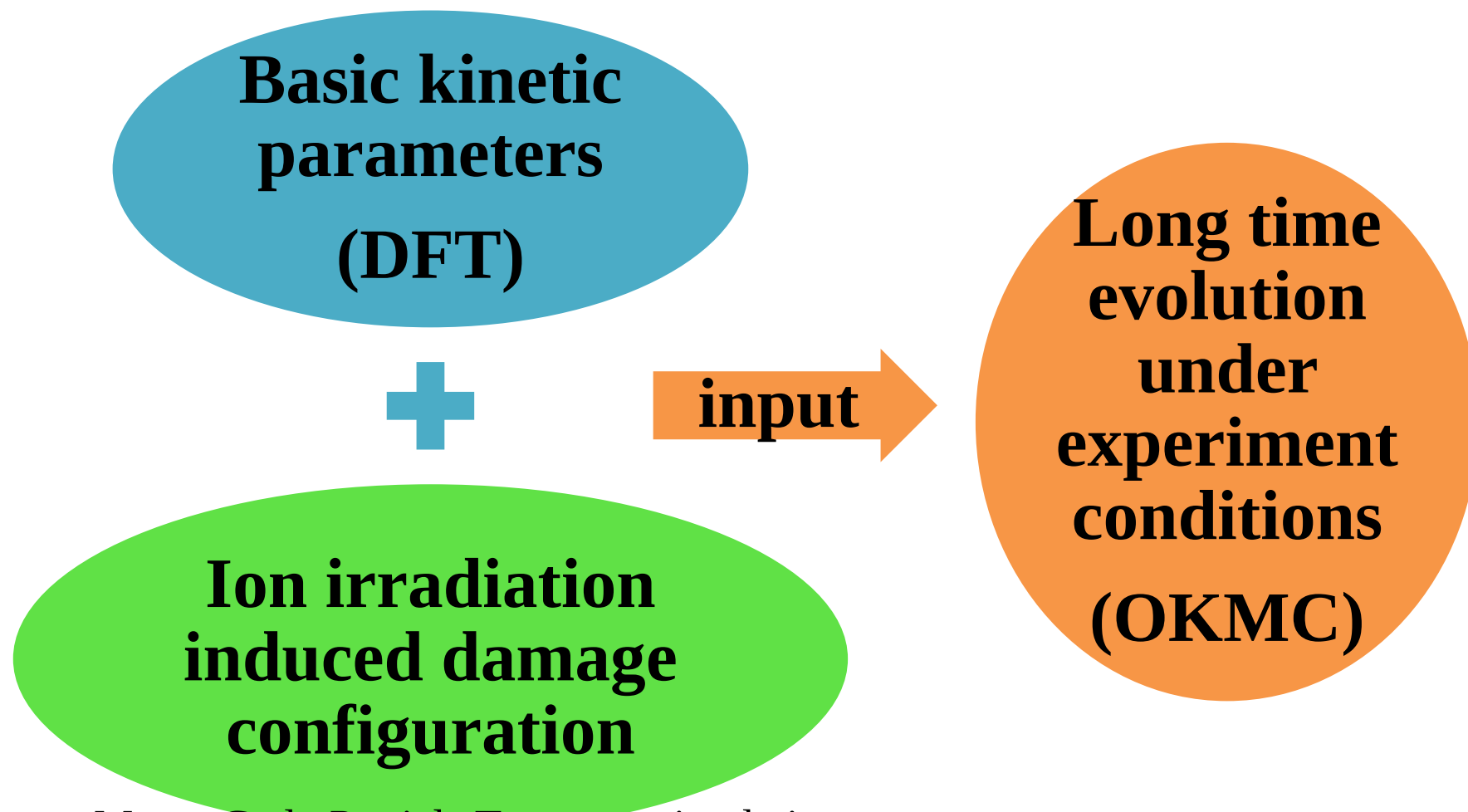
Experimental data for hydrogen retention and desorption in tungsten



Irradiation damage significantly increases the D retention in tungsten. (200eV vs 3keV). However, the experiment can not provide enough information to interpret the retention behavior.

Ogorodnikova J. Appl. Phys. 103, 034902

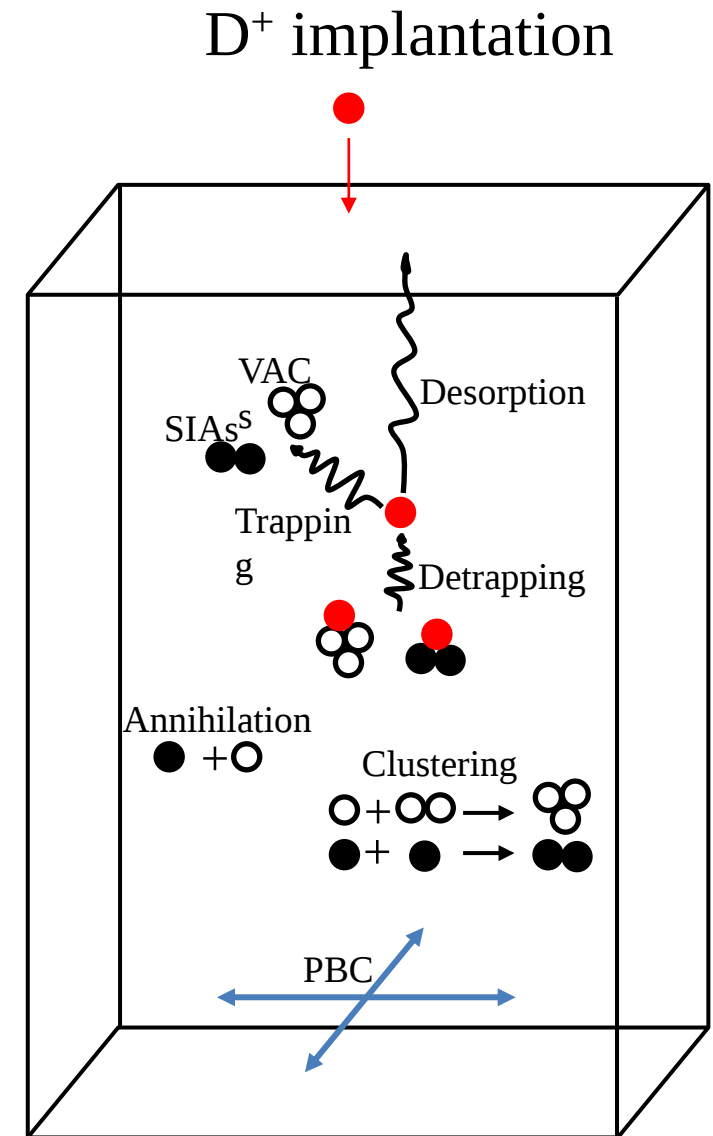
Computation method: Multi-scale model



Monte Carlo Particle Transport simulation
Using IM3D by Li and Zeng

In the our simulation, the program will randomly pick an event according to its reaction rate. Five different events are included:

- Damage created by ion irradiation (MC database)
- Defects migration
- Defects aggregation (clustering/annihilation)
- Point defect detrap from a defect cluster
- Defects absorbed by surface



Computation method: Key parameters adopted in our model:

Binding energy parameters:

n	$E^b(V_{n-1} + V_1)$	$E^b(V_1D_{n-1} + D_1)$	$E^b(V_2D_{n-1} + D_1)$	$E^b(I_{n-1} + I_1)$	$E^b(I_1D_{n-1} + D_1)$
1	/	1.19	1.39	/	0.33 ^[2]
2	-0.10 ^[1]	1.19	1.42	2.12 ^[1]	/
3	0.04 ^[1]	1.09	1.30	3.02 ^[1]	/
4	0.64 ^[1]	0.98	1.23	3.60 ^[1]	/
5	0.72 ^[1]	0.90	1.12	3.98 ^[1]	/
6	0.89 ^[1]	0.68	1.10	4.27 ^[1]	/
7	0.72 ^[1]	0.24	1.02	5.39 ^[1]	/
8	0.88 ^[1]	0.32	0.92	Capillary approximation ^[1]	/
9	Capillary approximation ^[1]	0.07	0.93		/
10		0.30	0.91		/
11		-0.01	0.58		/
12		0.36	0.66		/
>12	Capillary approximation				

^[1] C.S. Becquart J. Nucl. Mater. 403, 75

^[2] K. Heinola Phys. Rev. B 82, 094102

Capillary approximation:

$$E^b(V_{n-1} + V_1) = [E^b(V_1 + V_1) - E^f(V_1)] \left[n^{\frac{2}{3}} - (n-1)^{\frac{2}{3}} \right] / (2^{\frac{2}{3}} - 1) + E^f(V_1)$$

Computation method: Key parameters adoped in our model:

Migration parameters:

n	Migration energy E^m (eV)	Attempt frequency γ (THz)	Rotation energy E^r (eV)
V_n	$1.66^{[1]}$	$6 \times 1000^{1-n[1]}$	0
I_n	$0.013^{[1]}$	$0.013 \times n^{-0.5[1]}$	0.38 for $n=1^{[1]}$ Infinity for $n>1$
D_1	0.22	50.5	0
$V_n D_m$	infinity	0	infinity
$I_n D_m$	infinity	0	infinity

Note: D atoms are repulsive to each other, cannot form pure D-interstitial cluster in tungsten

^[1] C.S. Becquart J. Nucl. Mater. 403, 75

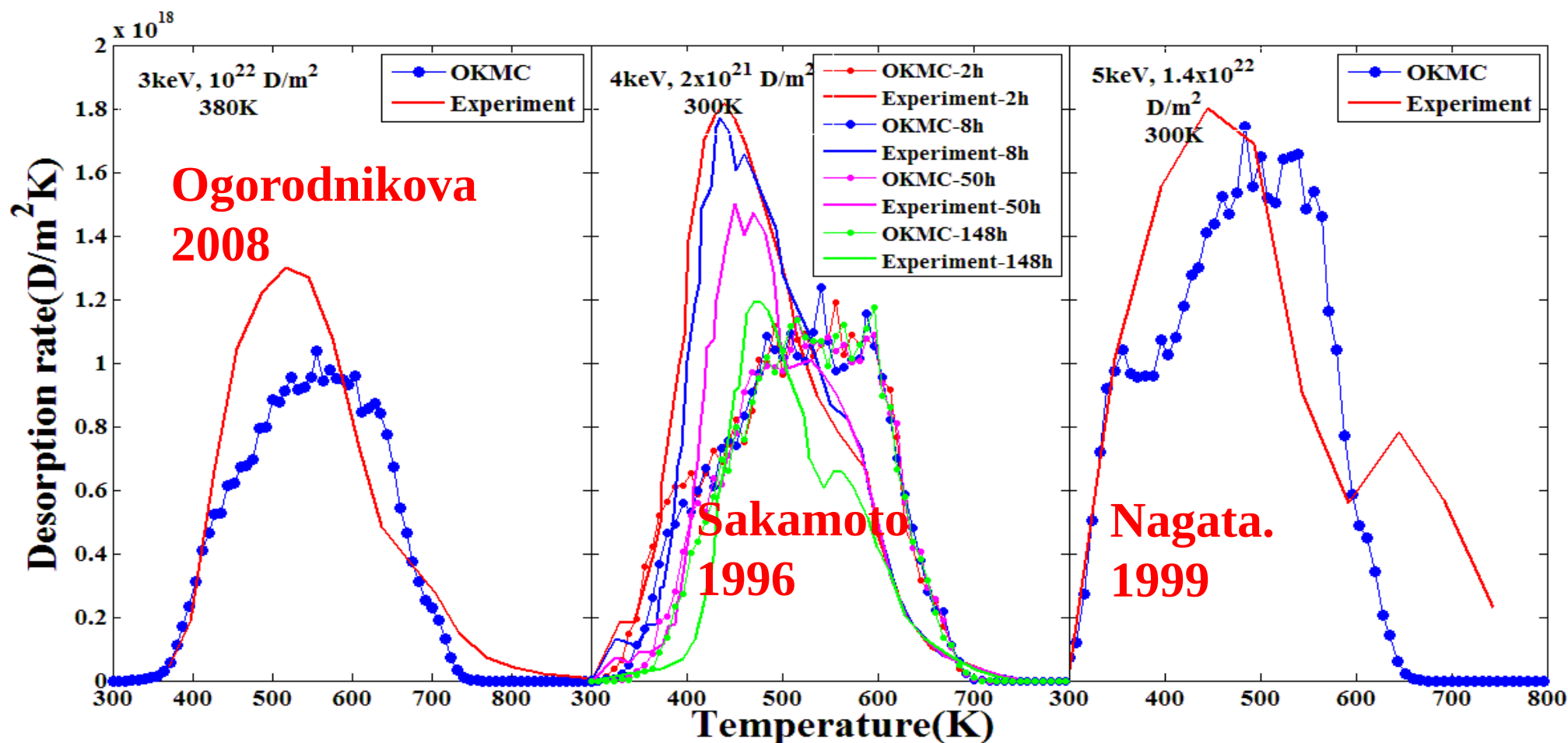
The simulations conditions are set up according to the published experiment work:

Reference	D ion energy (keV)	Fluence (D/m^2)	Implantation temperature (K)
Ogorodnikova. 2008 ^[1]	3	1×10^{22}	380
Sakamoto. 1996 ^[2]	4	1×10^{22}	300
Nagata. 1999 ^[3]	5	2.8×10^{22}	300

^[1] **J. Appl. Phys.** 103, 034902

^[2] **J. Nucl. Mater.** 233-237,776

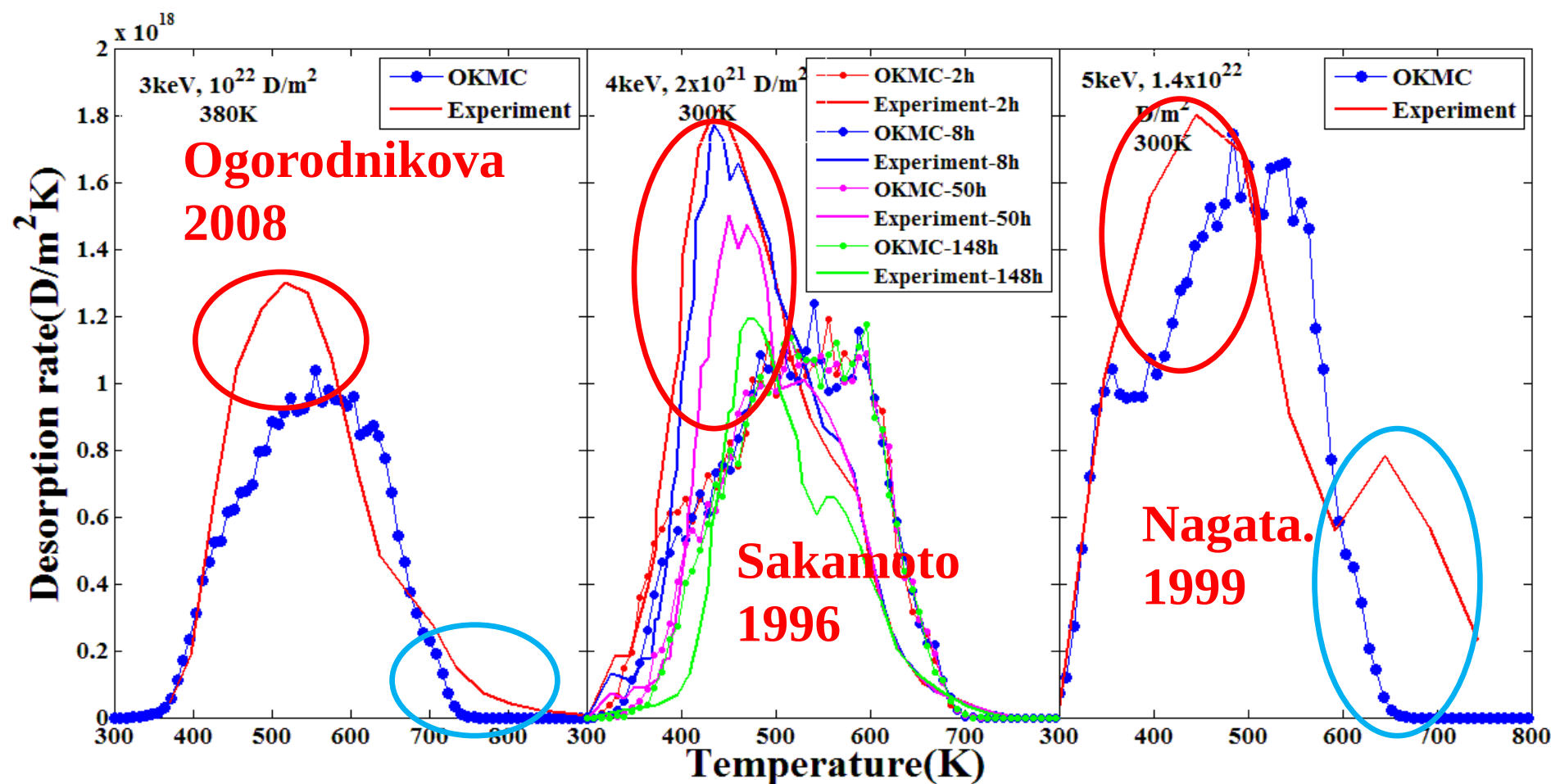
^[3] **J. Nucl. Mater.** 266-269,1151

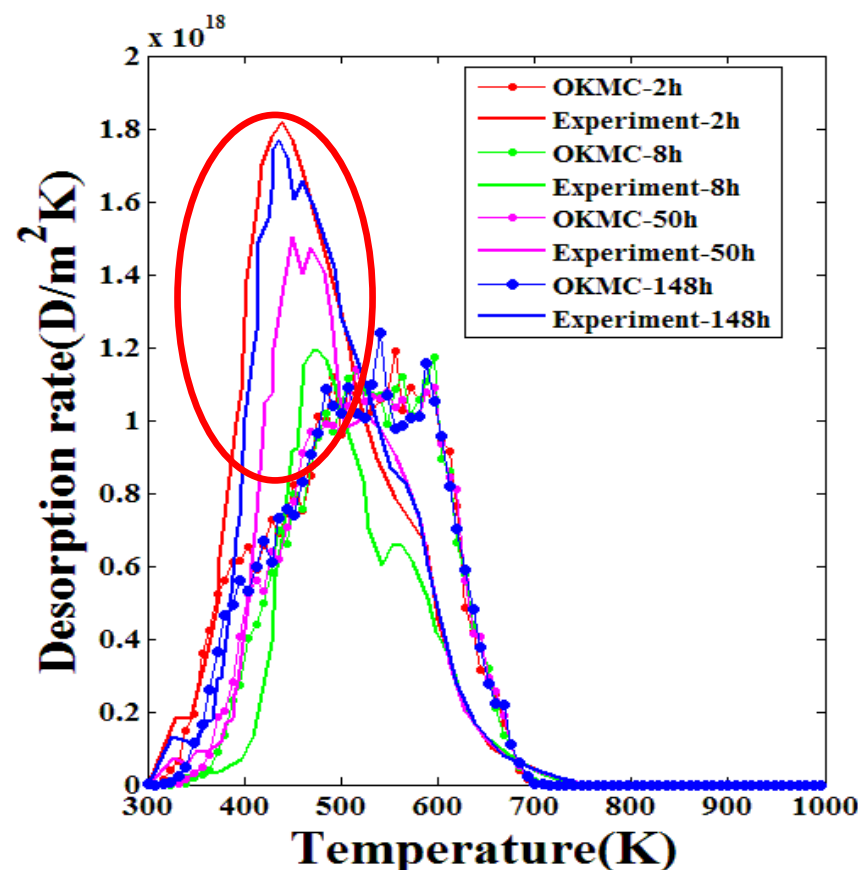
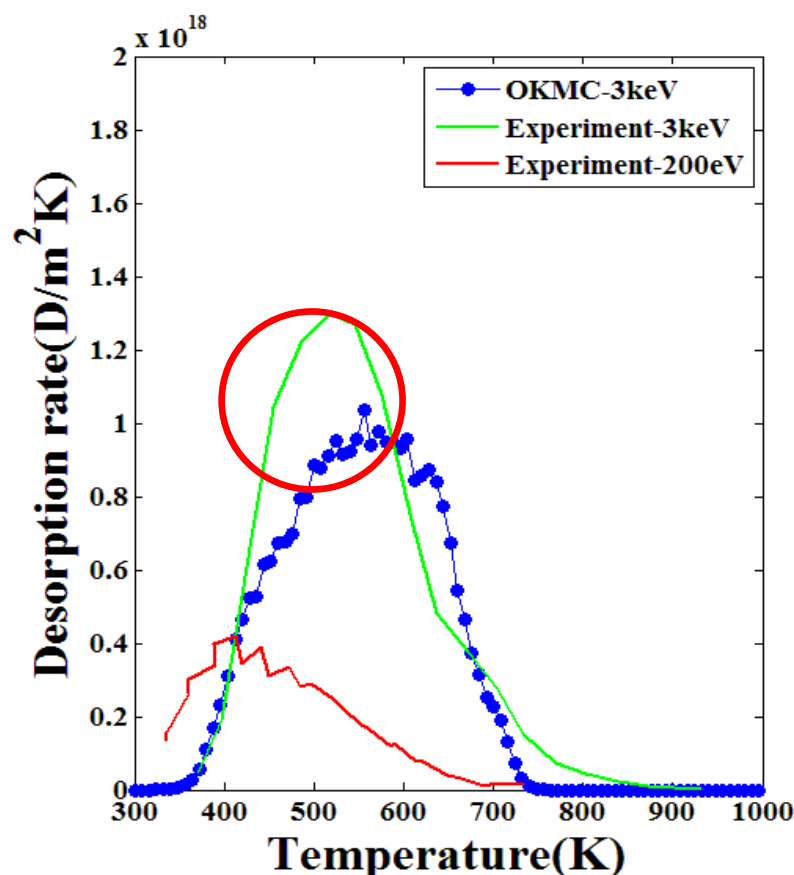


The simulated thermal desorption spectrum (TDS). The shape, location and height of simulated TDS are in a good agreement with experiment.

We also find some two kind of disagreement between simulation and experiment:

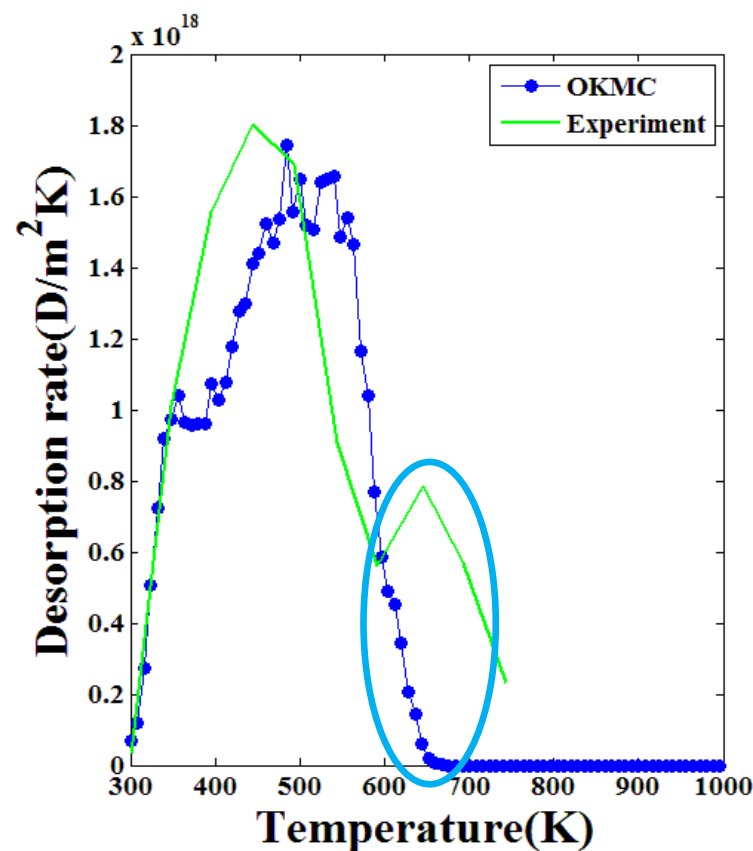
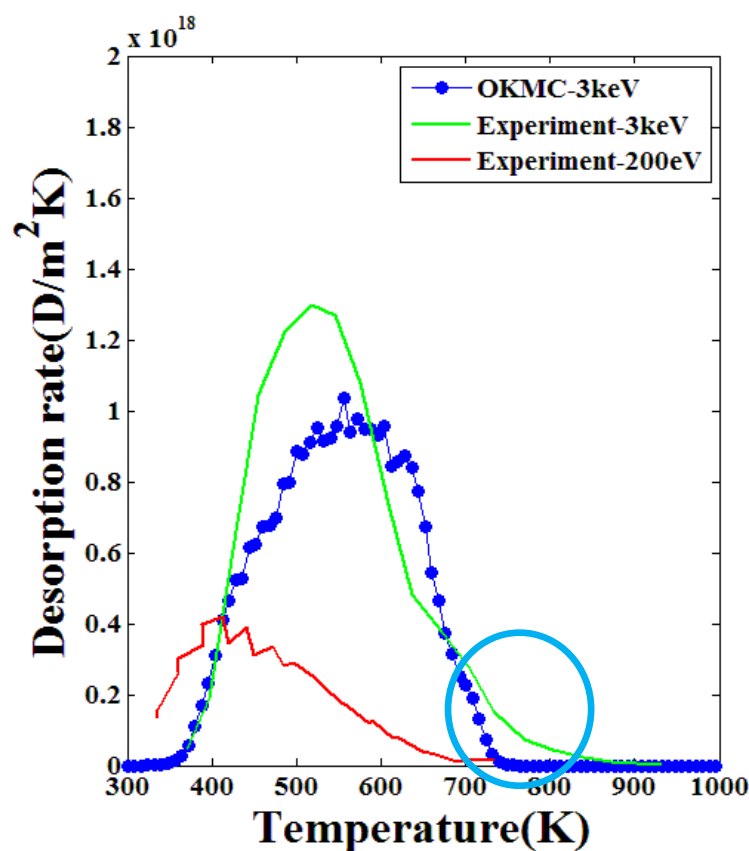
- Simulations slightly underestimate the desorption rate at temperature 400-500K.
- Present Simulation does not describe the high temperature desorption of the experiment.





Disagreement between 400-500K come from the intrinsic defects:

- The location and value of this discrepancy close to the spectrum of 200 eV implantation (no damage), in 200eV case, D atoms can only be trapped by intrinsic defects(impurity, dislocation, grain boundary...).
- A long time after implantation, this disagreement become obscure. Means that some D atoms are trapped weakly but deep from the surface, require more time to diffuse to the surface.



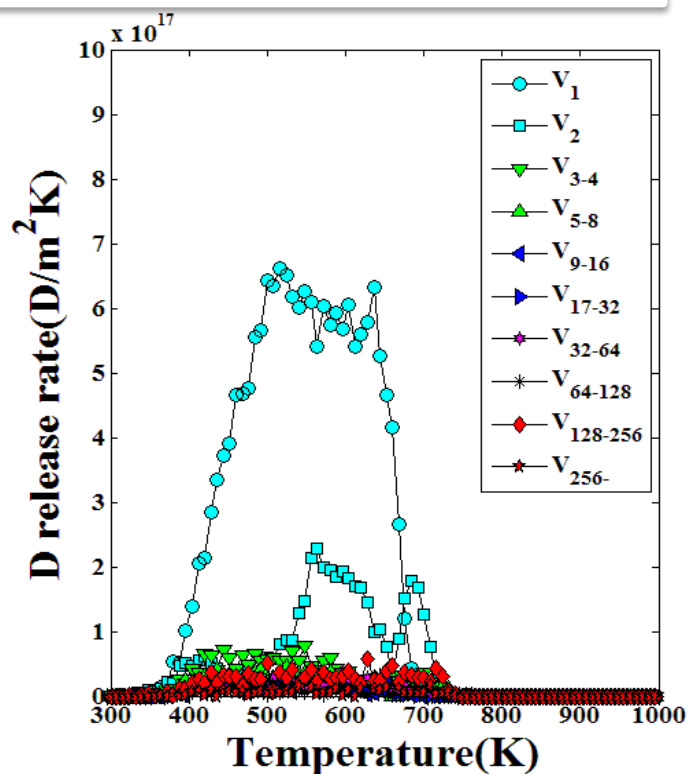
The corresponding trapping energy is 1.8~2.0 eV, close to the trapping of vacancy:

- Recent DFT shows hydrogen can reduce the migration barrier of vacancy ($E_m=1.6$ eV for V2, $E_m=0.7$ eV for V2H1), make vacancy easier to cluster.
- Stress field reduce the formation energy of vacancy ($E_f=3.2$ eV for strain free, $E_f=0$ eV for 20% strain). Allow implantation create more vacancy cluster.

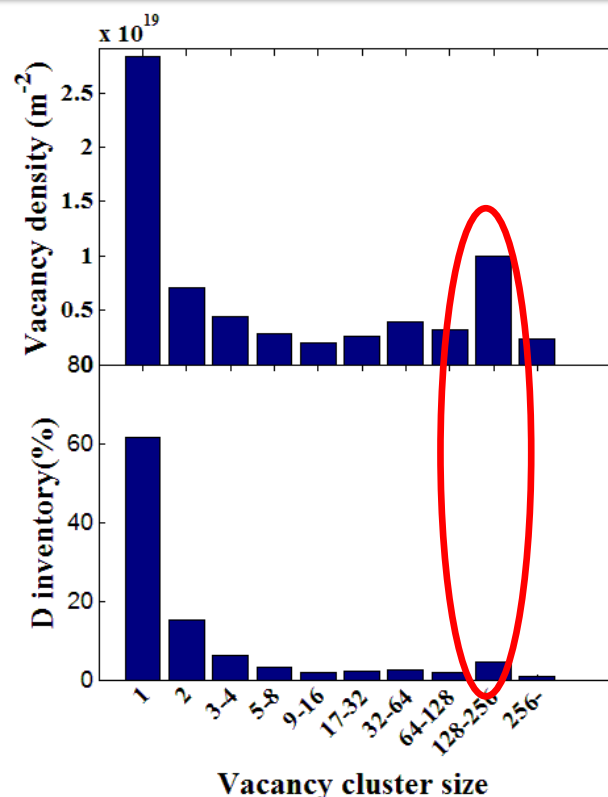
This two effect were not considered in our model,

therefore, **the desorption from vacancy cluster might have been underestimated.**

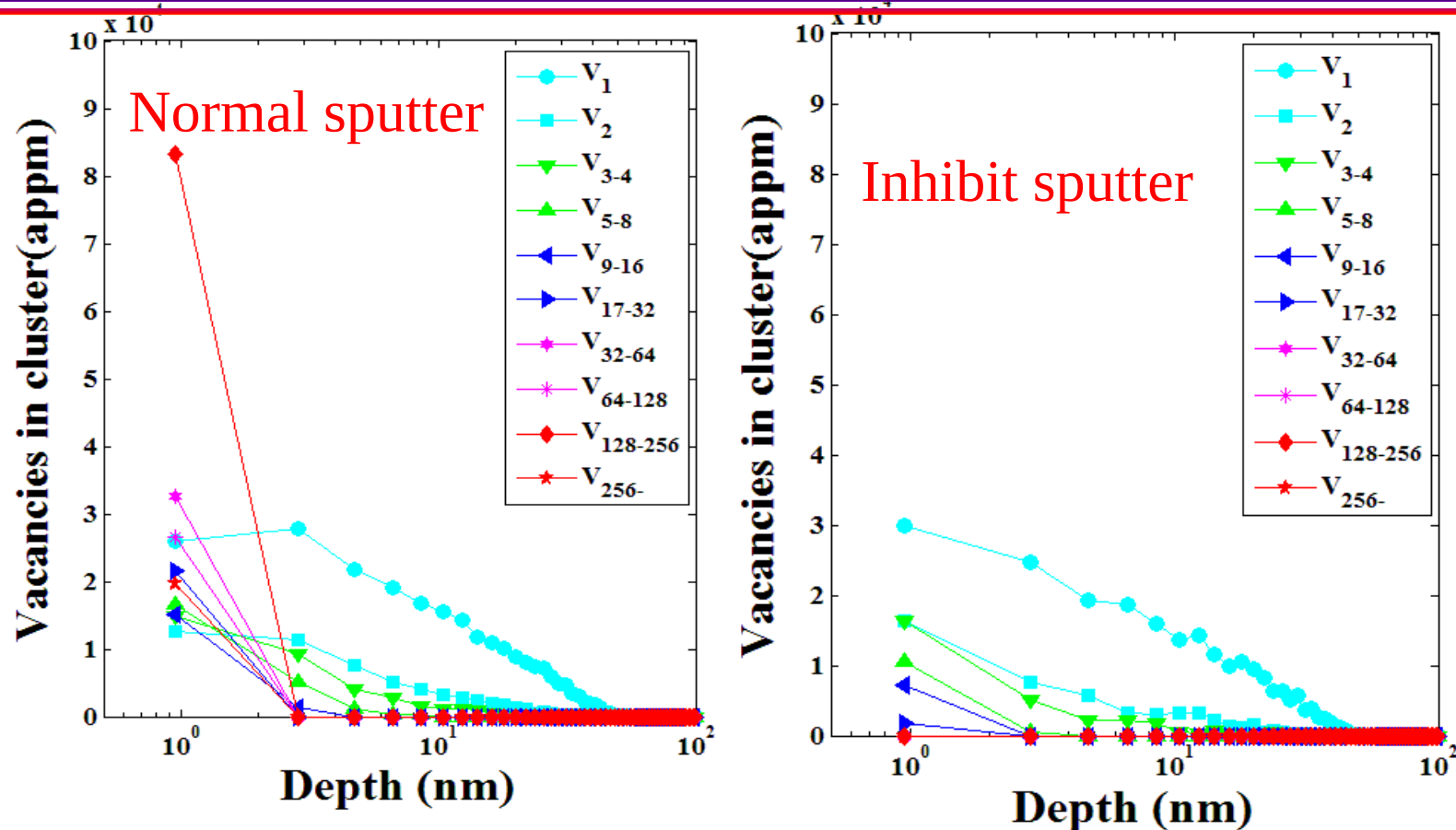
TDS for different cluster



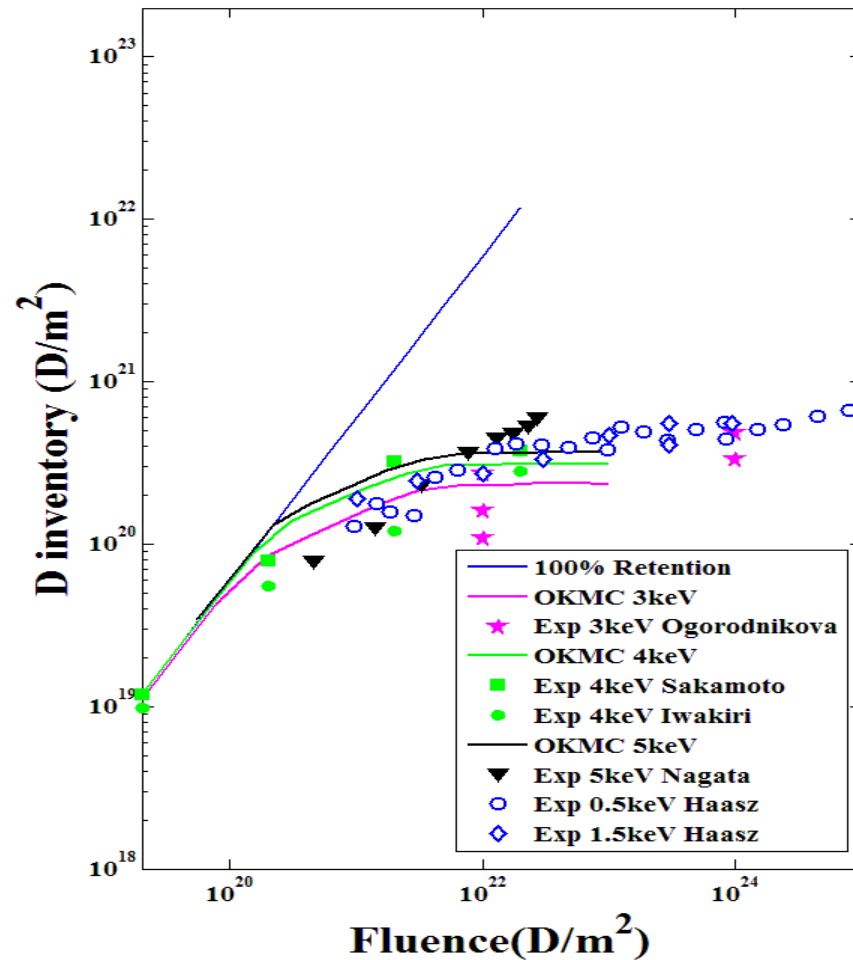
Contribution of different cluster



- Small vacancy clusters ($n \leq 4$) are the main trapping site of D.
- The present simulation shows an unexpected result: more frequent presence of $V_{128-256}$ make a important contribution.



To find out the reason of this abnormality, we analyzed the depth distribution of vacancies. We find large clusters localized in a few nanometer from the surface. As we know that sputtering can create net vacancy (no corresponding SIA), these vacancies can accumulate and form large cluster near the surface. If we inhibit the sputtering in our model, such large cluster vanished. This mechanism can lead to large vacancy clusters at low fluence, enhance the surface bubbling.



The saturation behavior detected in experiment is also found in the simulation .

- The multi-scale model is capable of simulating the D retention experiments. Simulated results are in good agreements with experiments. Also, it can provide the information that cannot be obtained from the experiment. (TDS analysis, sputtering enhanced bubbling)
- In the high energy (above threshold energy) D implantation experiments, D atoms are mainly trapped by small vacancy clusters ($n \leq 4$). Corresponding to the desorption peak between 300~700K.
- The surface sputtering effect create net vacancies at the near surface region. These vacancies can accumulate and form large cluster at this region.

Thank you